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EXPERIMENTAL INVESTIGATION OF THE  
WET OXIDATION DESTRUCTION OF SHIP-  
BOARD WASTE STREAMS

Paul Schatzberg, et al

Naval Ship Research and Development Center  
Annapolis, Maryland

October 1974

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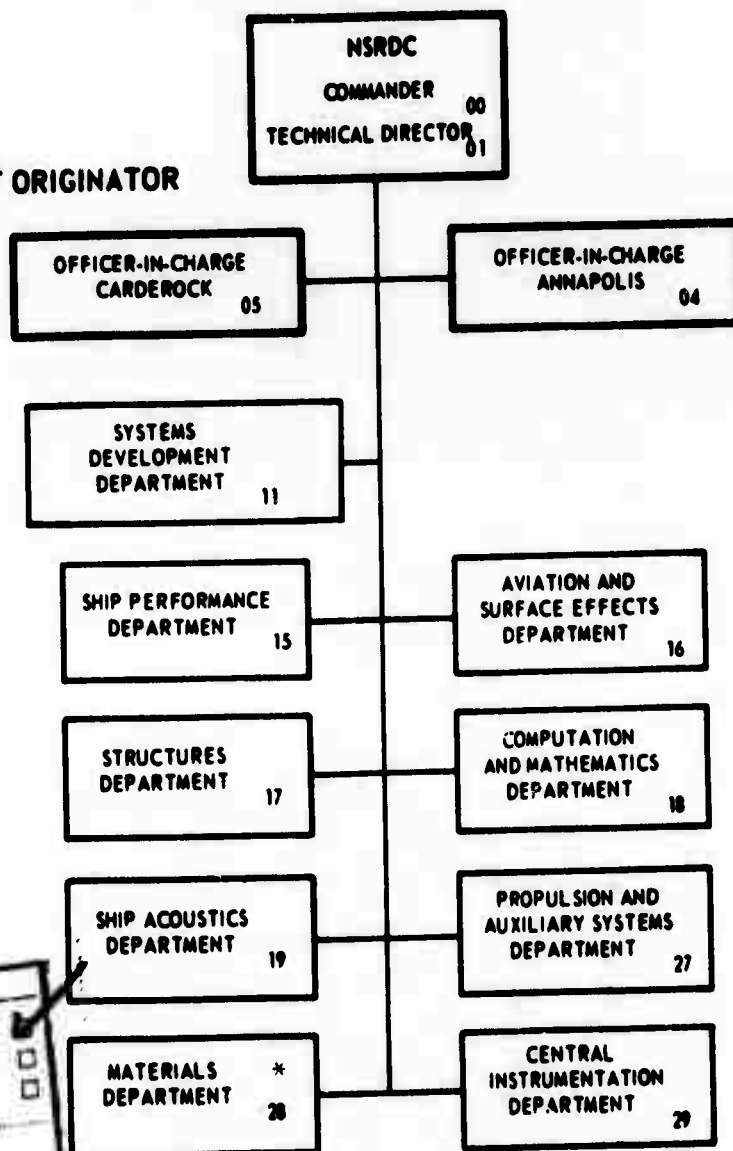
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## 20. ABSTRACT (Cont)

means for the ultimate destruction of organic wastes. This process was investigated by conducting experiments in a 1-gallon pressure vessel with a variety of wastes under different conditions. Waste types used in the experiments were sanitary, food, oil, municipal sludge, glucose, and cellulose. Results showed that the wet oxidation process obeys first-order kinetics consisting of two separate and distinct reactions. The first, a fast reaction, exhibits reaction rate constants ranging from 0.06 to 0.18 minute<sup>-1</sup>, while the second, a slower reaction, has reaction rate constants ranging from 0.003 to 0.008 minute<sup>-1</sup>. Catalysts have their main influence on the fast reaction, increasing its rate by a factor of three. Applying wet oxidation to destroy waterborne organic wastes consists in taking advantage of the fast reaction. Reduction in organic waste content, expressed as chemical oxygen demand, ranged from 60% to 85%, depending on the waste material, after 15 minutes of reaction time. The use of catalysts can increase this figure to 95%. Additional removal of organic matter can be achieved by further processing the wet oxidation effluent through a reverse osmosis membrane. The wide range of materials capable of being destroyed by wet air oxidation, the innocuous, sterile nature of the effluent, and its potential to be recycled for certain applications with little or no posttreatment make this process a candidate for the ultimate destruction of shipboard wastes.

#### ADMINISTRATIVE INFORMATION

This work was accomplished under Task Area SF 53 554 706 04, Task 16470, Work Unit 2861-120.

This report fulfills the requirements of milestone 4 of reference (a). A portion of this report was the basis of a technical paper, presented at the Fourth Intersociety Conference on Environmental Systems in Seattle, Washington, 29 July to 1 August 1974.

#### ADMINISTRATIVE REFERENCE

- (a) NSRDC Research Technology, Work Unit 2861-120, SF 53 554 706, Task 16470, May 1974

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## INTRODUCTION

Most waste water streams issuing from Navy ships are very dilute. This applies to sanitary (human), shower, lavatory, laundry, galley, and bilge water. Even when reduced volume flow equipment is employed, the resulting sanitary waste stream is 95% to 99% water. Nevertheless, the organic content of these waste streams pollutes the environment.

Continued unencumbered naval operations in United States and foreign harbors, navigable waters, contiguous zones and territorial waters are faced with increasingly stringent local, regional, national, and international water pollution abatement requirements. Consequently, at least some of the Navy's ships must have the capability for shipboard destruction of their wastes by 1980.

One way this can be achieved is by "burning" the waste in water. This is called wet oxidation, which is a process whereby organic wastes dissolved or suspended in water are converted to water, carbon dioxide, small amounts of low molecular weight organic acids, and a very small amount of fine inorganic ash. This process is conducted with an excess of oxygen at temperatures ranging from 475° to 600° F\* in a pressure vessel which maintains the water as a liquid. Air overpressure can range from 50 to 300 lb/in<sup>2</sup>.\*\* The resulting operating pressures range from approximately 600 to 1850 lb/in<sup>2</sup>.

Advantages of this process are:

- Aqueous waste streams, such as those identified above, are converted directly into sterile, innocuous effluents. No known pathogenic microorganisms survive under these conditions.
- Energy requirements are substantially less than for incineration, since only a small amount of the water being treated converts to steam.
- Oxidation of the organic waste releases heat, so that the process can be thermally self-sustaining.

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\*Abbreviations used in this text are from the GPO Style Manual, 1973, unless otherwise noted.

\*\*All pressures mentioned in this report will be expressed in pounds per square inch gage, unless specifically noted otherwise.

- The process is relatively rapid and is particularly suitable where space is at a premium.

- Essentially no contaminants are released to the atmosphere.

- The effluent water after minimal posttreatment, such as filtration to remove inorganic ash, is adequate for selected reuse, such as sanitary flush or laundry. Flash distillation of the hot effluent water has potential for higher quality reuse application.

Disadvantages of the process are:

- It is conducted at elevated pressures.

- Materials of construction for the pressure vessel and auxiliary equipment must be carefully selected to be corrosion resistant.

- Heavy-duty air compressors are required to supply air against the operating steam pressure.

Results of experiments in wet oxidation presented in this report are intended to enhance understanding of the process, identify its limitations, and provide technology leading to shipboard application of the process.

#### BACKGROUND

The commercial application of wet oxidation for the destruction of sewage sludge and other organic wastes has been reviewed and investigated.<sup>1</sup> Current effort in wet oxidation for shipboard application involves two recently completed U.S. Coast Guard contracts for a prototype pilot plant processing dilute sewage consisting of sanitary, laundry, shower, lavatory, and galley wastes from a crew of 10 to 20 men.<sup>2,3</sup> In addition, the U.S. Navy has recently awarded a contract<sup>4</sup> for the construction of its first land-based wet oxidation plant capable of destroying spent propellants as well as industrial and domestic wastes. A research contract,<sup>5</sup> issued by the U.S. Navy, to conduct small-scale wet oxidation pilot plant processing

<sup>1</sup>Superscripts refer to similarly numbered entries in the Technical References at the end of the text.



experiments with several shipboard wastes, has been completed. The application of wet oxidation for the destruction of wastes generated in a space station is being investigated as part of a NASA contract.<sup>6</sup> The National Materials Advisory Board of the National Academy of Sciences has recently completed an investigation of materials of construction for wet oxidation pressure vessels intended for shipboard application.<sup>7</sup> As a result of significant advancement in wet oxidation technology for shipboard application, the Navy has recently procured two closed-loop (no discharge) shipboard systems for treatment of sanitary wastes.<sup>8</sup> A laboratory evaluation of one of these systems will be conducted here.

#### APPARATUS AND EXPERIMENTAL PROCEDURES

Experiments were conducted in a 1-gallon pressure vessel (Serial N71-1740, Autoclave Engineers, Inc., Erie, Pennsylvania), equipped with an electric heating jacket and magnetic drive stirring assembly, fitted with a hollow stirring shaft and two impellers for air dispersion and mixing. A schematic diagram of the apparatus is shown in figure 1. The autoclave was constructed of Hastelloy B. A liner and all internally wetted parts of the autoclave were constructed of either Hastelloy B or C. A second liner and set of internally wetted parts for the autoclave were made of commercially pure titanium, to be used during experiments in which an especially high acid concentration was expected.

Six different waste feeds were employed for the wet oxidation experiments: concentrated sanitary waste from a reduced flush sanitary waste collection system, tomato juice as simulated food waste, oil-in-water emulsions, sludge from the underflow of a primary clarifier of a municipal wastewater treatment plant, glucose solutions, and paper (cellulose) slurries. The feeds required various means of preparation ranging from manual shaking, macerating with a blender to ultrasonic mixing before being suitable for injection into the autoclave. Appendix A provides additional detail on the waste feed materials used. The main variables examined in these experiments in addition to feed type included temperature, oxygen content, reaction rate, pH, and effect of salt water.

In most cases, experiments were conducted in the same manner. The autoclave was charged with the predetermined amount of water, air, or oxygen, and the heater was turned on. Stirring rate was maintained at 1000 r/min.

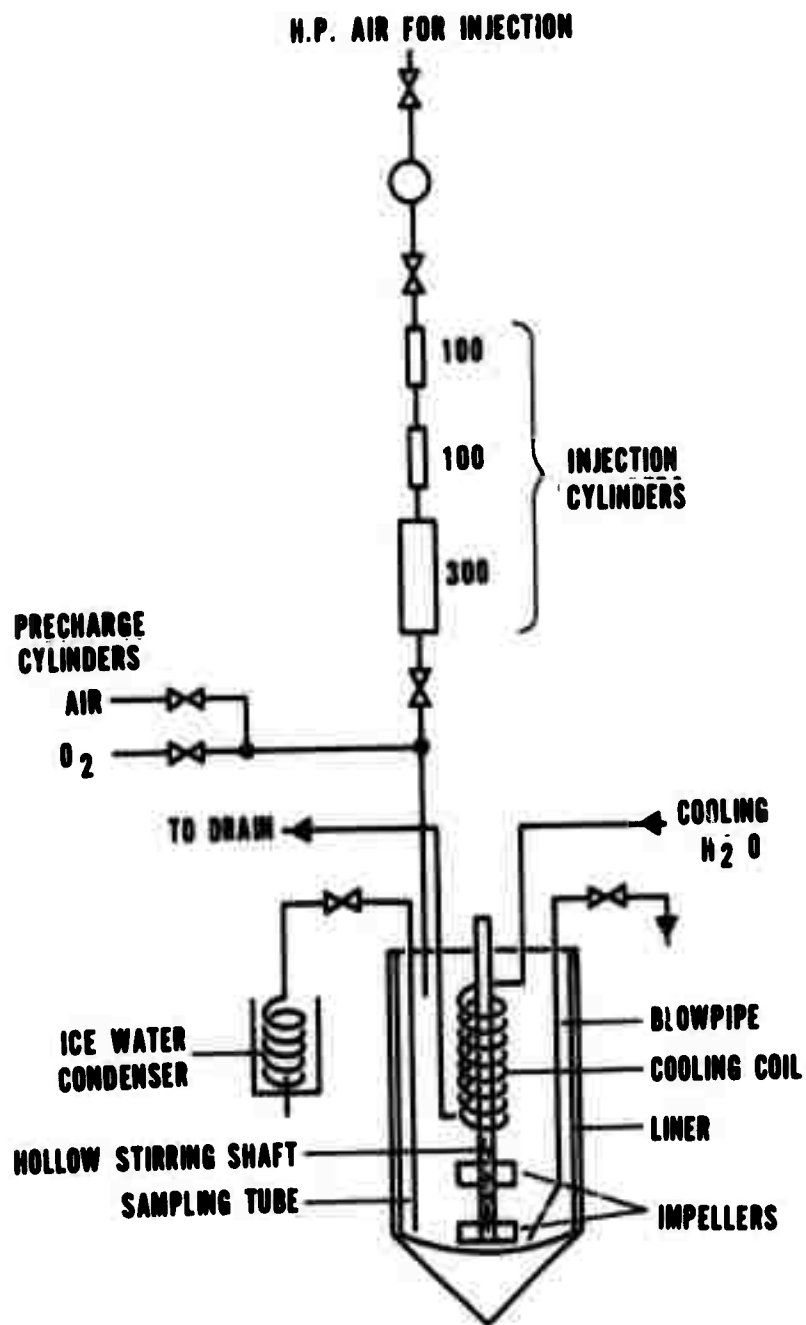


Figure 1  
Wet Oxidation Apparatus

The feed was placed in the injection cylinders, usually including a 100-ml distilled water flush in the last cylinder. When the autoclave reached the desired operating temperature and pressure, the feed was rapidly injected by using high-pressure air. This established a sharply defined experiment starting point. Samples were removed from the vessel at designated time intervals, beginning at 30 seconds and continuing to 90 minutes from the time of feed injection. The samples were then analyzed for chemical oxygen demand (COD) according to the procedure in Standard Methods.<sup>9</sup> A more detailed operating procedure for the experiment is described in appendix B.

## RESULTS

### CHEMICAL OXYGEN DEMAND

The most direct procedure for presenting the effectiveness of the wet oxidation process is in terms of the percent reduction in COD as a function of time. This is illustrated in figure 2, which shows the time-dependent degree of destruction of various wastes. Each data point is the arithmetic mean obtained from a number of runs conducted with each feed type at 500° F. The number of runs is shown in the figure. Detailed results of each individual experiment, including calculated arithmetic means and standard deviations, are presented in appendix C. Table 1 presents the summarized results of many runs with the feed types arranged in order of decreasing difficulty of destruction. Cellulose is the easiest to destroy, while the most difficult material is the reduced flush sanitary waste, probably due to its high urine content. Examination of the variances from which the standard deviations are derived for the reduction in COD shows, in general, that variance decreases significantly with time. This is illustrated in table 2. The large variance early in a wet oxidation experiment is caused partly by the large relative error in removing a sample from the autoclave at the precise time period indicated, but may also be influenced by the complexity of the oxidation reactions occurring. As the oxidation progresses, the concentration of large molecules being oxidized decreases, and the concentration of low molecular weight carboxylic acids, primarily acetic acid, increases.<sup>2</sup> Since the samples taken after the first 10 minutes of the wet oxidation process consist of the low molecular weight compounds, whose oxidation process is simpler, the repeatability of the COD determination improves as shown by the decrease in variance.

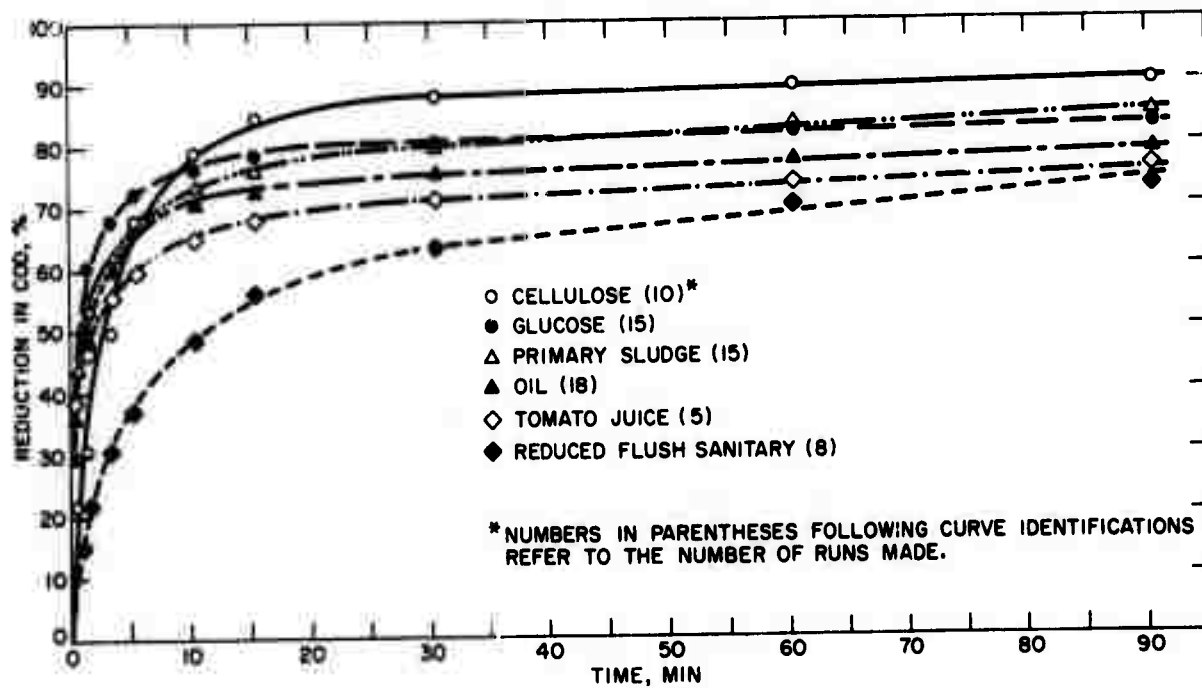


Figure 2  
 Wet Oxidation of Various Feeds  
 at 500° F (Combined Runs)

TABLE 1  
WET OXIDATION OF VARIOUS FEEDS AT 500° F (COMBINED RUNS)

Waste	Reduction in COD, % at				Number of Runs	Range of Initial COD mg/l
	15 Min	Standard Deviation	60 Min	Standard Deviation		
Concentrated sanitary	56	8	70	5	8	1,310-1,980
Tomato Juice	68	3	74	2	5	9,090-10,880
Oil-in-water emulsion	73	9	78	7	18	2,810-4,310 7,670-12,850
Primary sludge	76	7	83	5	15	1,720-3,890
Glucose	77	4	81	3	15	9,030-14,540
Cellulose	85	9	90	7	10	400-1,440

TABLE 2 - VARIANCE IN REDUCTION OF  
CHEMICAL OXYGEN DEMAND FOR PRIMARY SLUDGE  
AT 500° F (see Table 1-C, Appendix C, 15 Runs)

Elapsed time, min	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5
Mean % reduction in COD	43.8	53.6	62.2	68.4	73.2	76.4	80.1	82.9	84.5
Standard deviation	14.5	12.7	11.3	10.4	7.5	6.6	5.5	5.2	5.1
Variance	210	161	128	108	56	44	30	27	26

## REACTION KINETICS

The chemistry of wet oxidation has been shown to obey first-order kinetics with respect to the organic matter present.<sup>1</sup> Thus:

$$-\frac{dC}{dt} = k_1 C, \quad (1)$$

where  $C$  is the concentration of organic wastes usually expressed as the COD in milligrams per liter, and  $k_1$  is the specific reaction rate constant. Equation (1) states that the rate of decrease (destruction) of the wastes is proportional to the concentration of the wastes. (First-order kinetics for this process is valid only when an excess of oxygen is maintained throughout the reaction.)

Rearranging equation (1) and integrating yields:

$$\ln \frac{C_0}{C} = k_1 t, \quad (2)$$

where  $C_0$  is the concentration of organic wastes at the start of the reaction. Equation (2) can be expressed graphically by plotting the logarithm of  $C_0/C$  against time  $t$ . The slope of the resulting straight line can be used to calculate the specific reaction rate constant  $k_1$ .

The course of the wet oxidation reaction can be illustrated by plotting the percent COD reduction in figure 2 as a function of time. A perhaps more effective way of presenting the data is to utilize equation (2). Figures 3 through 10 present the data in this fashion, along with the percent COD reduction for comparison. A smooth curved line can be drawn through all the data points in these figures. However, linear fits with good correlation coefficients can be obtained. Instead of a single straight line, as might be expected from equation (2), two or three straight lines can be fitted to the data, the lines having progressively smaller slopes and therefore smaller values of the specific reaction rate constant. In order to provide for uniform analysis and comparison of the data, the first four data points, ranging from 0.5 to 10.5 minutes after initiation of the reaction were fitted to one straight line, while the subsequent data points were fitted to a second line. Observation of the data points in figures 3 through 10 shows that three linear plots could also have been constructed. The specific reaction rate constant,  $k_1$ , is determined from the slope of the first line, while  $k_2$  is determined from the slope

of the second line. It is clear the  $k_2$  is always smaller than  $k_1$  for this reaction. Results presented in figures 3 through 10 show that regardless of feed type at least two major reactions occur. These can be adequately modelled as two consecutive first order reactions with separate rate constants. The first of these is rapid, involving the hydrolysis and oxidation of large molecules, such as proteins, carbohydrates, and cellulose. This results in the formation of water, carbon dioxide, and low molecular weight organic residues consisting primarily of acetic acid and its homologs.<sup>2</sup> The wet oxidation of these organic residues occurs at a much lower rate and is the second of these reactions. The concept of two consecutive reactions is supported by pH data presented later in the report, acidity being a measure of the reaction progress.

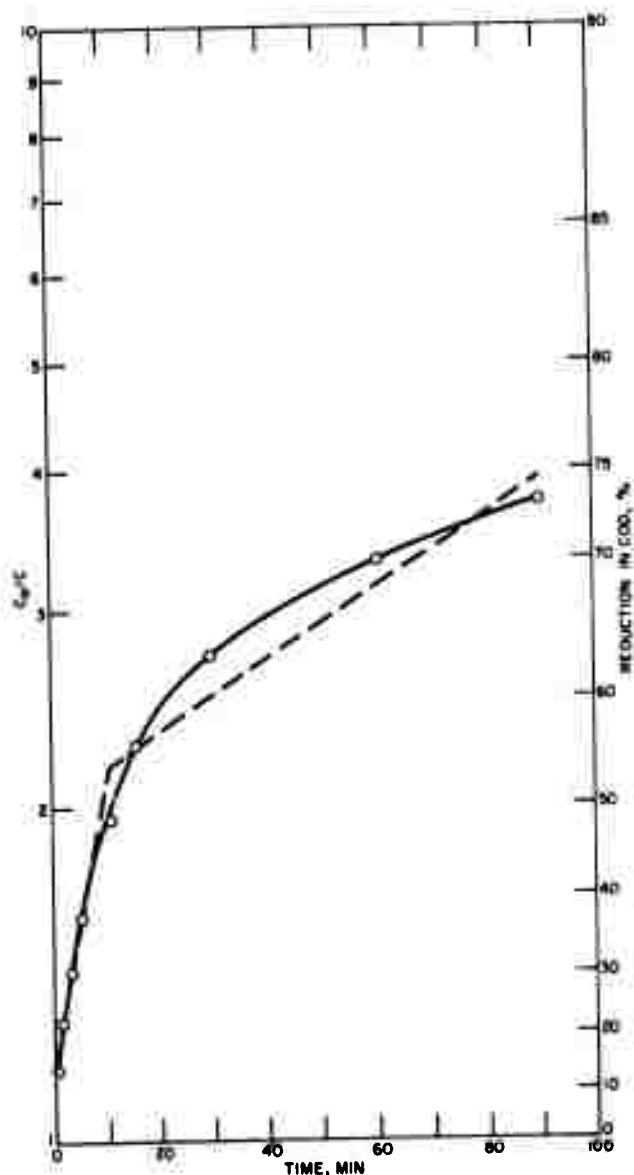


Figure 3  
Wet Oxidation of  
Concentrated Sanitary Waste  
(500° F, 8 Runs)

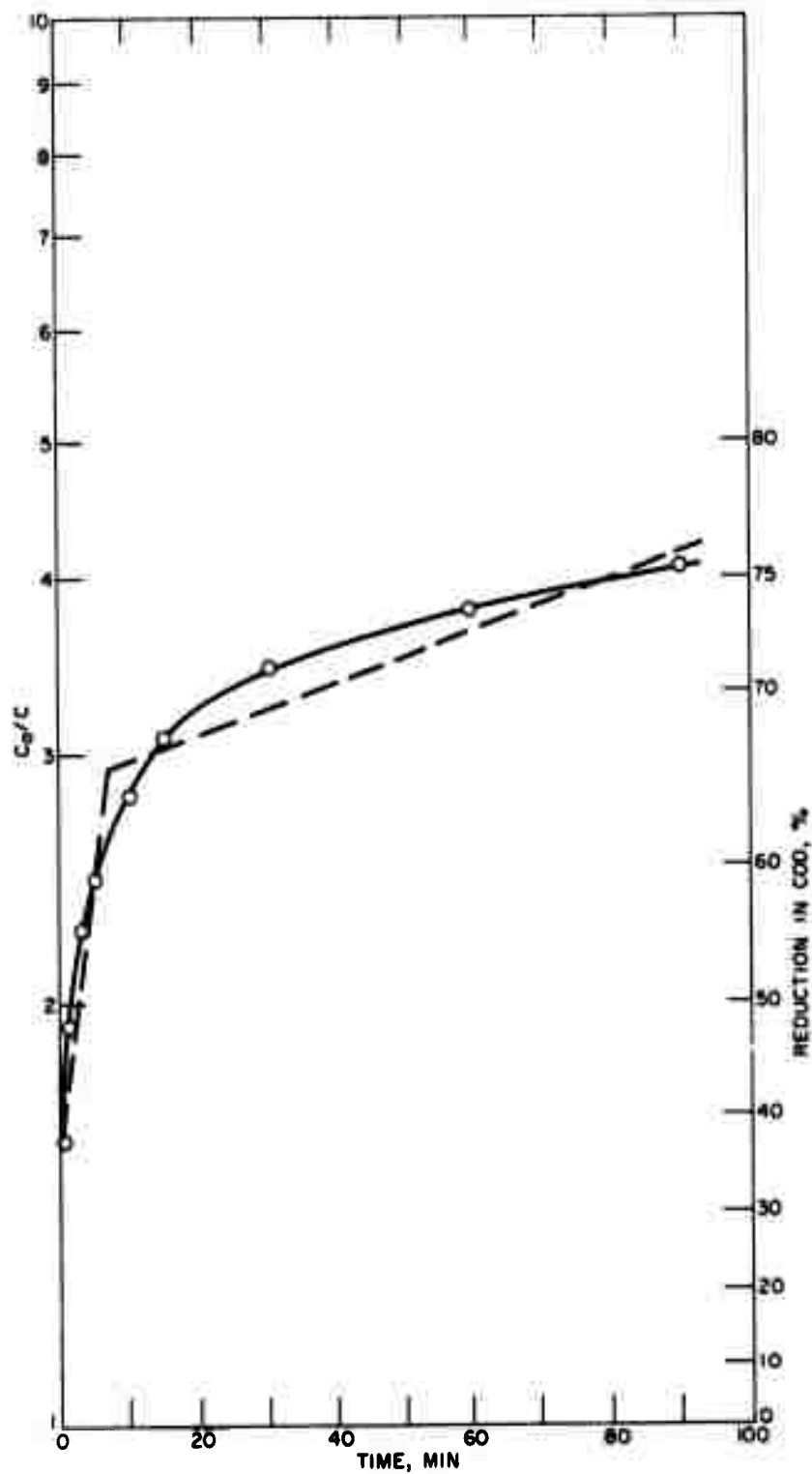


Figure 4  
Wet Oxidation of Tomato Juice  
(500° F, 5 Runs)



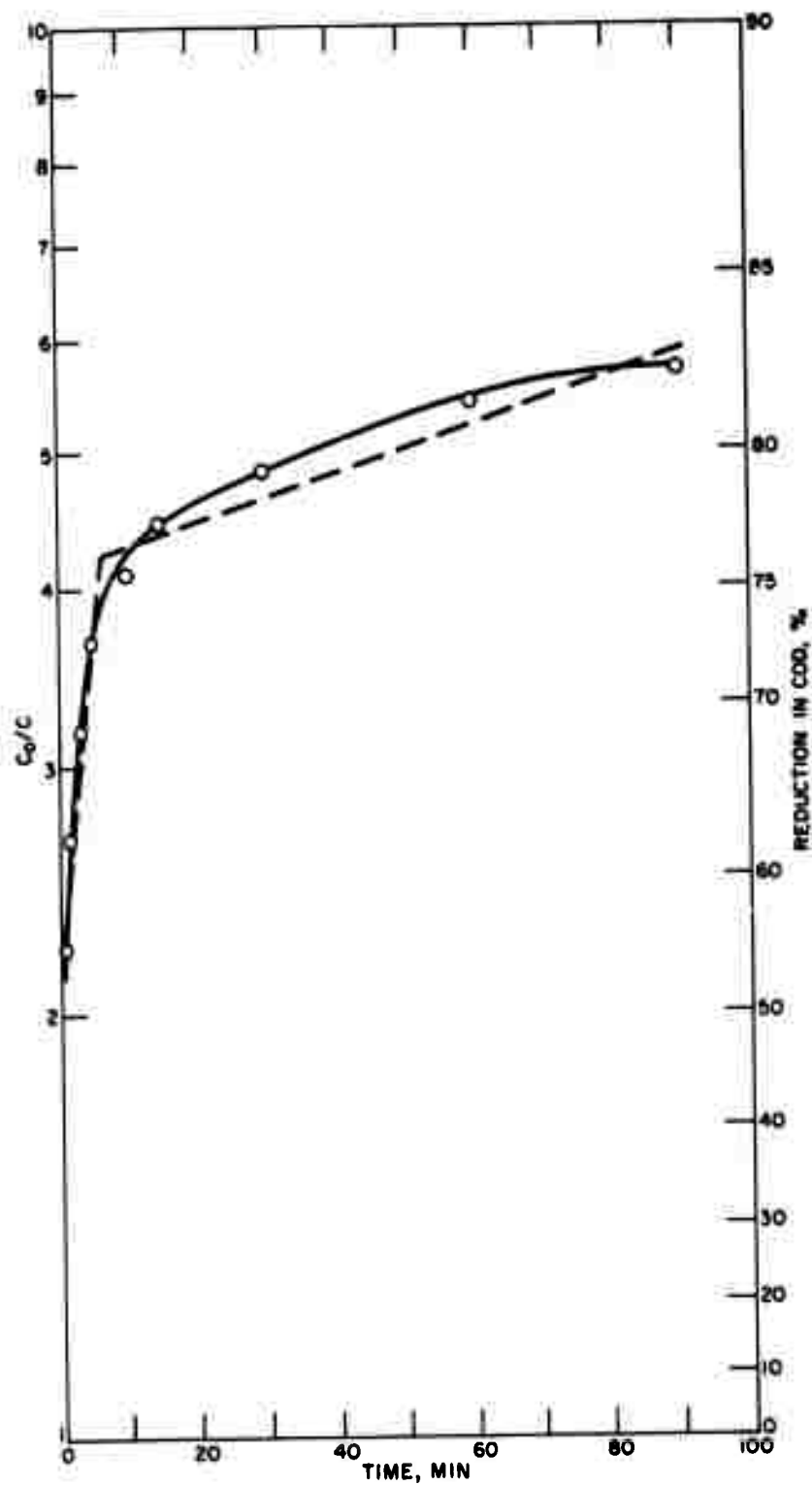


Figure 5  
Wet Oxidation of Oil-in-Water  
Emulsions (500° F, 0.1%, 5 Runs)

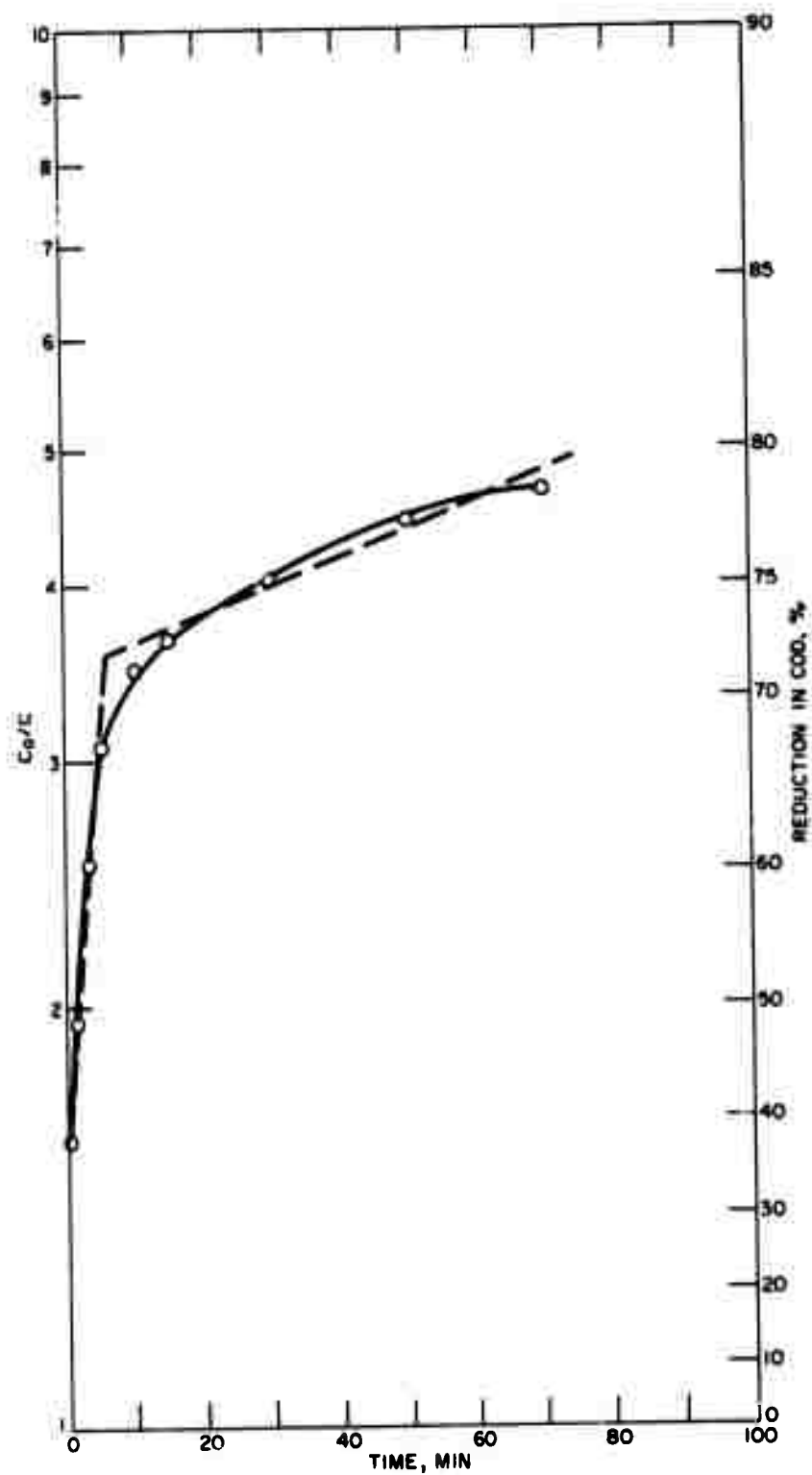


Figure 6  
Wet Oxidation of Oil-in-Water Emulsions  
(500° F, 0.5%, 13 Runs)

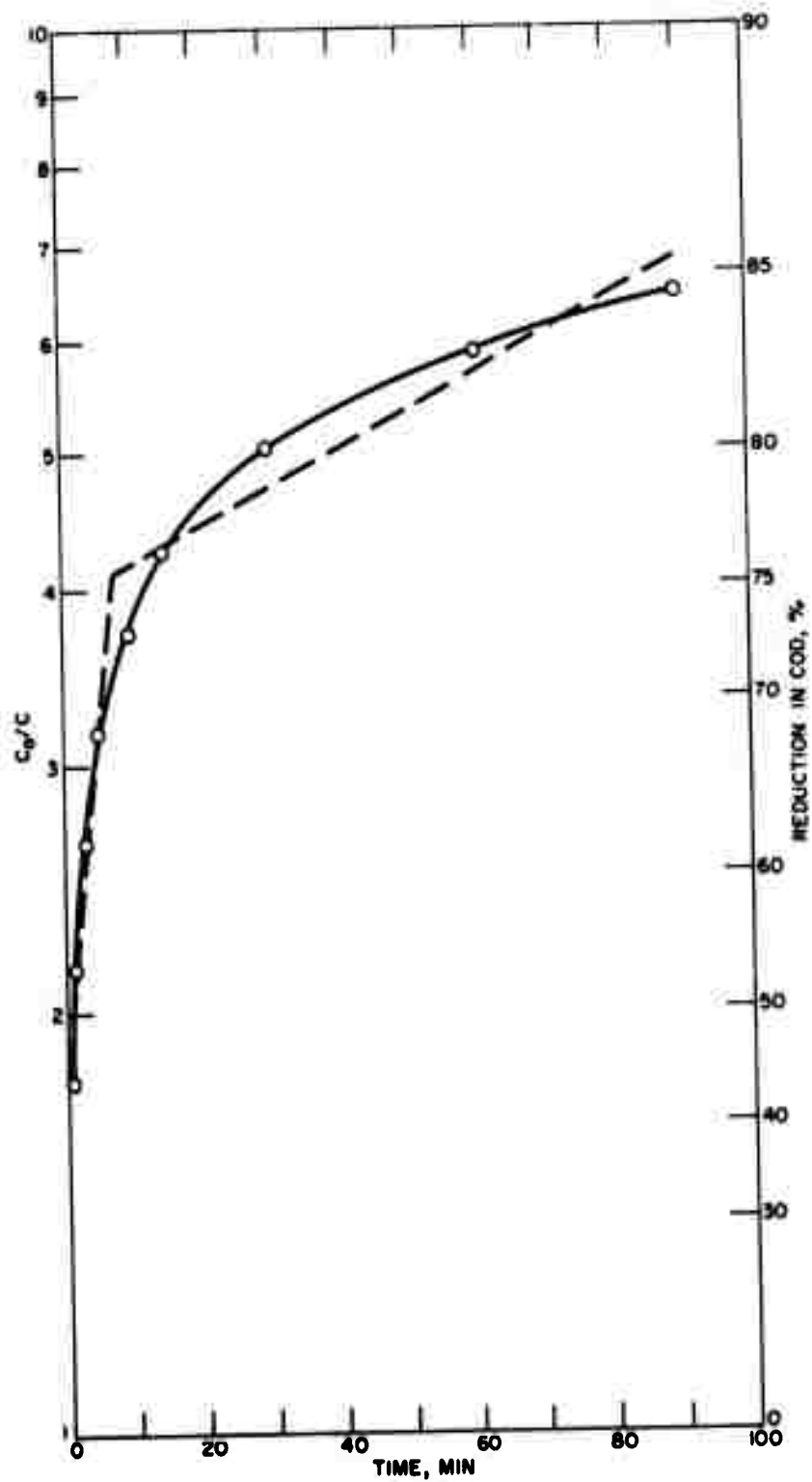


Figure 7  
Wet Oxidation of Primary Sludge  
(500° F, 15 Runs)

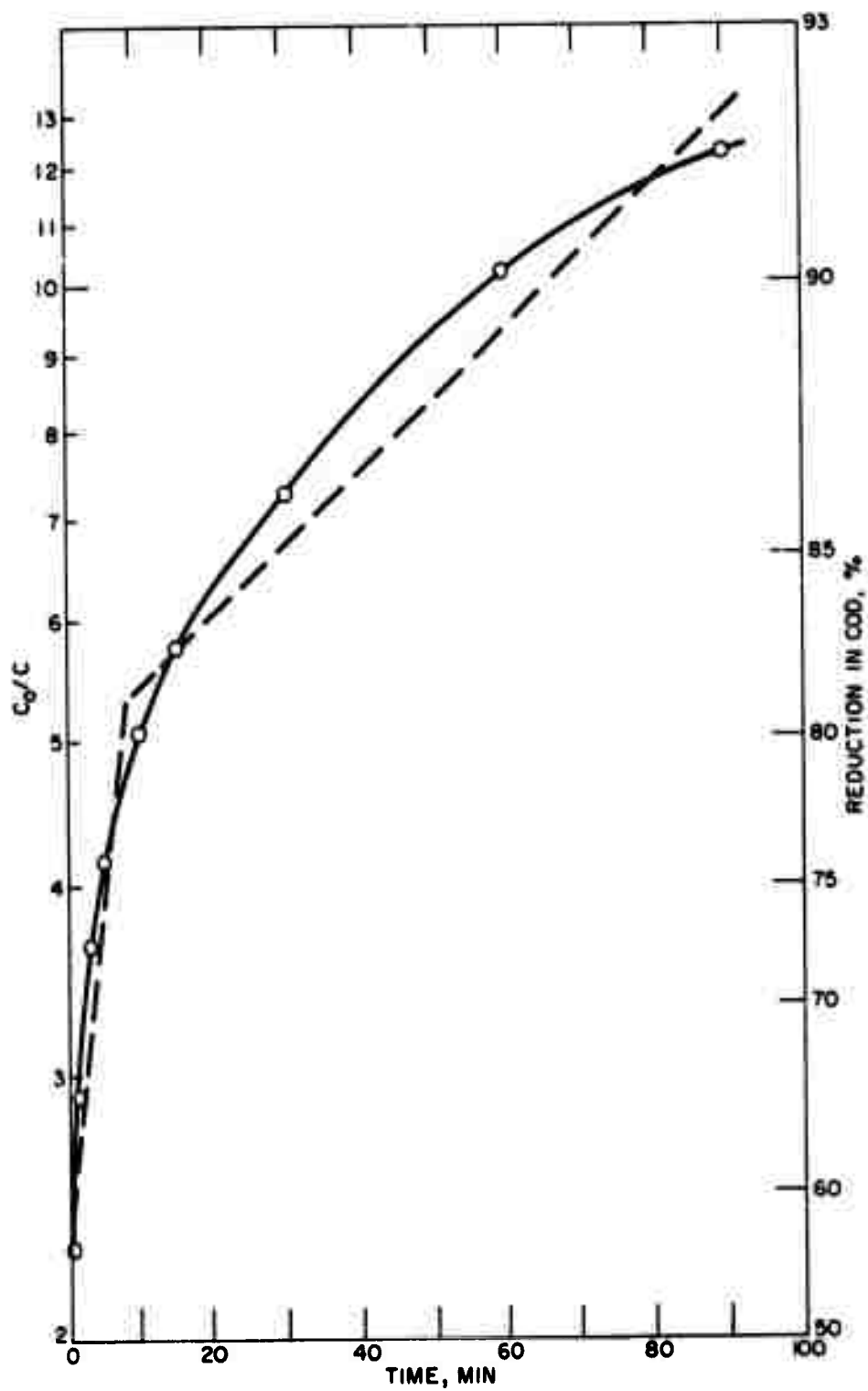


Figure 8  
Wet Oxidation of Primary Sludge  
(600° F, 11 Runs)

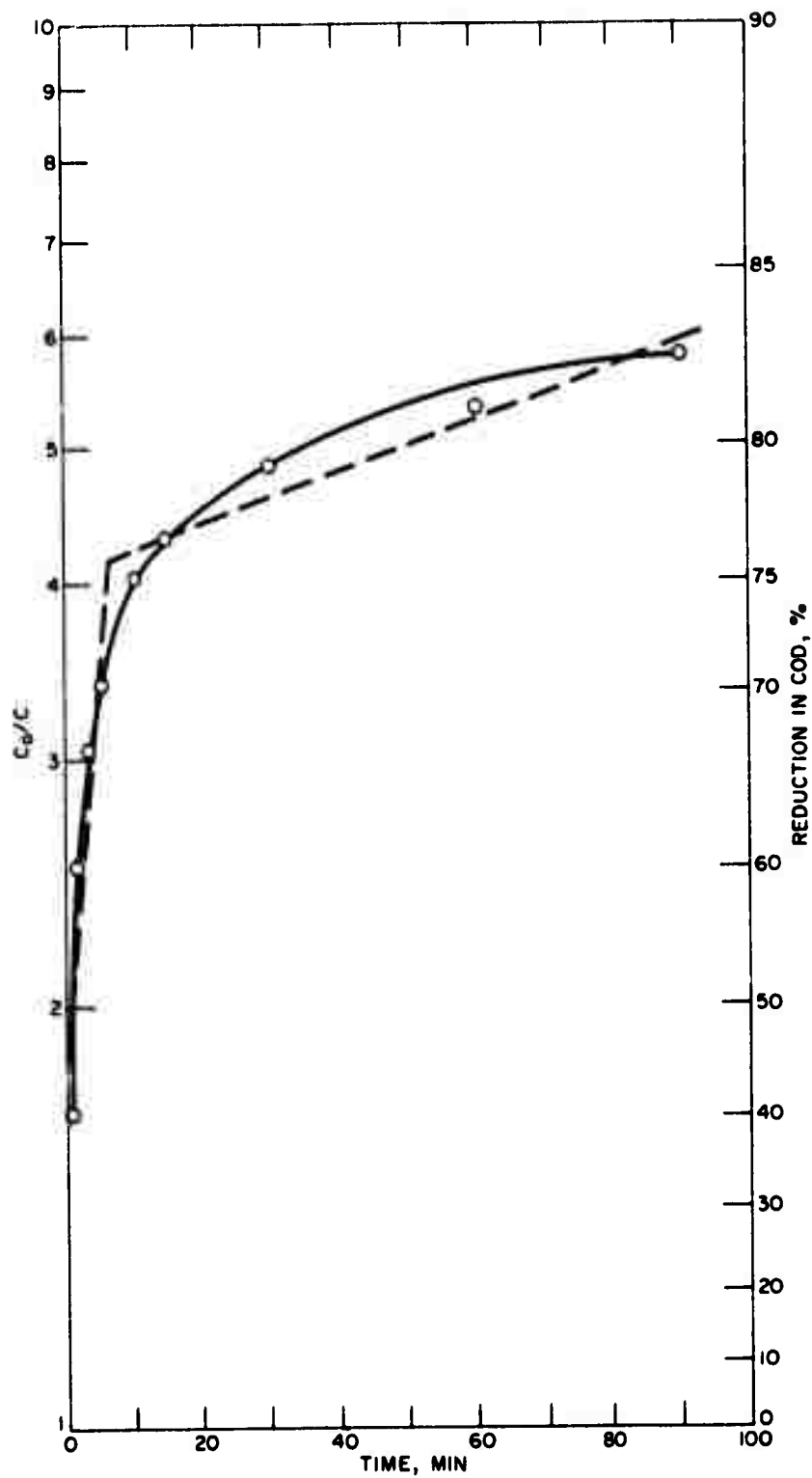


Figure 9  
Wet Oxidation of Glucose  
(500° F, 14 Runs)

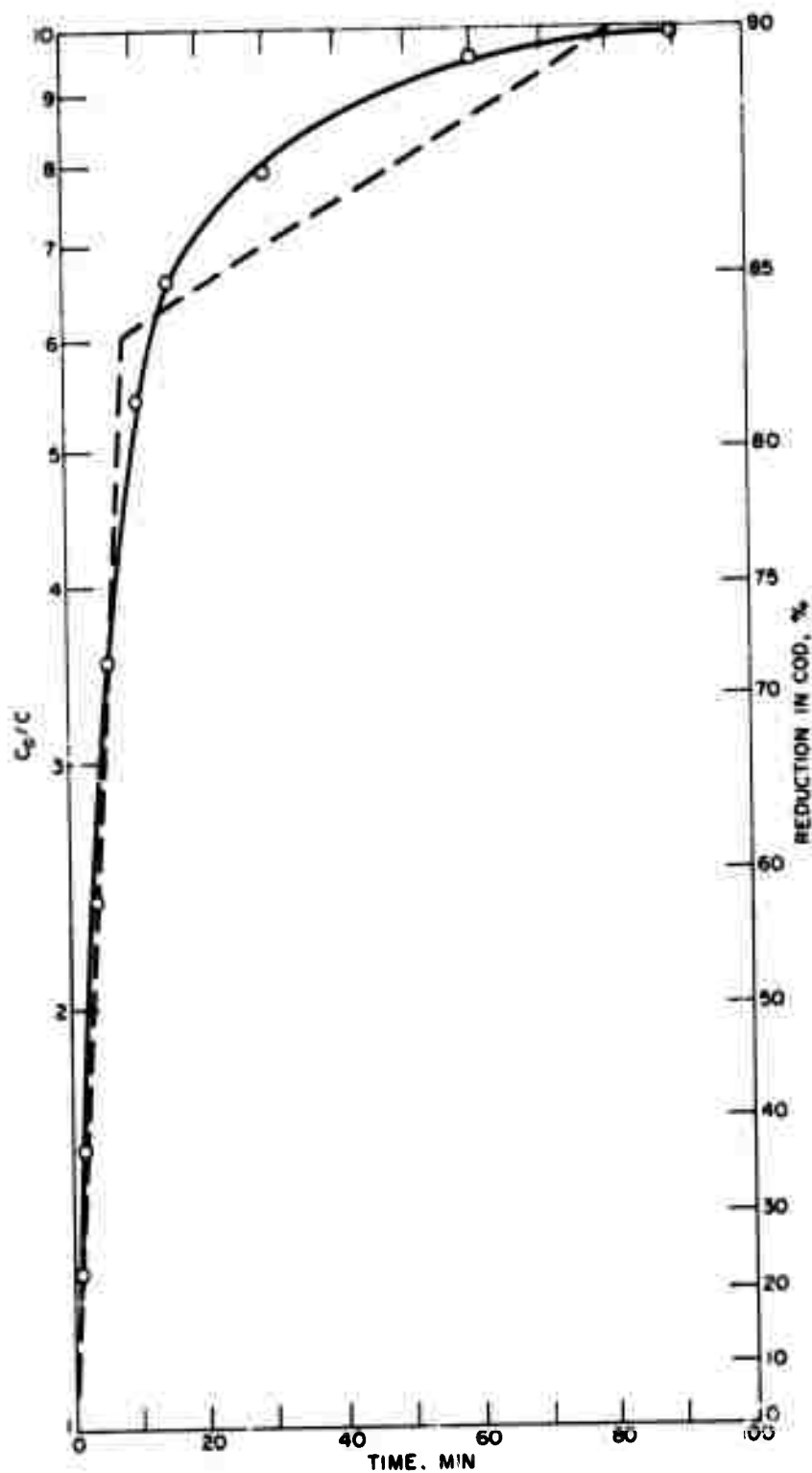


Figure 10  
Wet Oxidation of Cellulose Slurries  
(500° F, 10 Runs)

Reaction rate constants calculated from the slopes of the linear plots in figures 3 through 10 are presented in table 3. The distinction between the fast and slow reactions is further illustrated by the ratio of  $k_1/k_2$ , where  $k_1$  and  $k_2$  are the specific reaction rate constants for the fast and slow reactions, respectively. The waste types in table 3 are arranged in the same order as they are in table 1. This order was determined from the percent reduction in COD obtained after 15 minutes of wet oxidation. It is seen from table 3 that this order is approximated by the values of  $k_1$ . Results of all reaction rate constants calculated, their arithmetic means, standard deviations, and ranges are given in appendix D.

TABLE 3  
AVERAGE SPECIFIC REACTION RATE CONSTANTS  
FOR VARIOUS WASTES WET OXIDIZED AT 500° F

Waste	$k_1, \text{min}^{-1}$ (fast)	$k_2, \text{min}^{-1}$ (slow)	$k_1/k_2$	No. of Runs
Concentrated sanitary	0.06	0.008	7.5	8
Tomato juice	0.07	0.004	17.5	5
Oil, 0.1% in water	0.11	0.004	27.5	5
Oil, 0.5% in water	0.14	0.003	47.0	13
Primary sludge <sup>(1)</sup>	0.12	0.007	17.0	15
Glucose	0.13	0.004	32.0	14
Cellulose	0.18	0.007	26.0	10

(<sup>1</sup>) Primary sludge wet oxidized at 600° F resulted in an average  $k_1$  of 0.11  $\text{min}^{-1}$  and  $k_2$  of 0.011  $\text{min}^{-1}$  based on 11 experiments.

## INFLUENCE OF OXYGEN

Wet oxidation must be conducted with an excess of oxygen to maximize reaction rate and prevent the formation of carbon. Table 4 shows the ratios of oxygen available at various pressures to oxygen demand, as affected by COD level. In most experiments a substantial excess of oxygen was present. Both dissolved and gaseous oxygen participate in the wet oxidation process. At high temperatures and pressures, oxygen is very soluble in water, as seen from table 5. The amount of excess oxygen remaining throughout each of two typical experiments conducted with primary sludge at 500° F is shown in tables 6 and 7.

TABLE 4  
RATIOS OF OXYGEN AVAILABLE  
AT VARIOUS PRESSURES TO CHEMICAL OXYGEN DEMAND

COD, mg/l	Precharge Pressure, lb/in <sup>2</sup>					
	100 O <sub>2</sub>	200 O <sub>2</sub>	300 O <sub>2</sub>	400 O <sub>2</sub>	500 O <sub>2</sub>	500 Air
1,000	19.3	38.6	57.9	77.2	96.5	17.5
2,000	9.6	19.3	29.0	38.6	48.2	8.8
3,000	6.4	12.9	19.3	25.7	32.2	5.8
4,000	4.8	9.6	14.5	19.3	24.1	4.4
5,000	3.9	7.7	11.6	15.4	19.3	3.5
6,000	3.2	6.4	9.6	12.9	16.1	2.9
7,000	2.8	5.5	8.3	11.0	13.8	2.5
8,000	2.4	4.8	7.2	9.6	12.1	2.2
9,000	2.1	4.3	6.4	8.6	10.7	1.9
10,000	1.9	3.9	5.8	7.7	9.6	1.8
11,000	1.8	3.5	5.3	7.0	8.8	1.6
12,000	1.6	3.2	4.8	6.4	8.0	1.4
13,000	1.5	3.0	4.4	5.9	7.4	1.3
14,000	1.4	2.8	4.1	5.5	6.9	1.2
15,000	1.3	2.6	3.9	5.1	6.4	1.2



TABLE 5  
SOLUBILITY OF OXYGEN IN WATER<sup>10, 11</sup>

Temperature ° F	Precharge Pressure lb/in <sup>2</sup>	Partial Pressure O <sub>2</sub> at Operating Temperature lb/in <sup>2</sup>	Solubility	
			ml O <sub>2</sub> /g H <sub>2</sub> O	mg O <sub>2</sub> /l H <sub>2</sub> O
500	100	180	0.8	1150
500	300	540	2.4	3450
500	500	900	3.5	5000
600	100	200	1.4	2000
600	300	600	4.2	6000

TABLE 6  
OXYGEN REMAINING, PRIMARY SLUDGE  
500° F (EXPERIMENT 11202)

Time min	Reduction %	COD Removed mg/l	COD Remaining mg/l	O <sub>2</sub> Remaining mg/l	Ratio of O <sub>2</sub> :COD Remaining	Fraction of O <sub>2</sub> Remaining
0.0	0.0	0	3090	57,900	18.7	1.00
0.5	64.7	2000	1090	55,900	51.3	0.96
1.5	74.4	2300	760	55,600	73.2	0.96
3.5	84.1	2600	510	55,300	108.4	0.96
5.5	87.4	2700	370	55,200	149.2	0.95
10.5	84.1	2600	460	55,300	120.2	0.96
15.5	87.4	2700	360	55,200	153.3	0.95
30.5	90.6	2800	280	55,100	196.8	0.95
60.5	93.8	2900	190	55,000	289.5	0.95
90.5	97.1	3000	130	54,900	422.3	0.95

TABLE 7  
OXYGEN REMAINING, PRIMARY SLUDGE  
500° F (EXPERIMENT 11102)

Time min	Reduction %	COD Removed mg/l	COD Remaining mg/l	O <sub>2</sub> Remaining mg/l	Ratio of O <sub>2</sub> :COD Remaining	Fraction of O <sub>2</sub> Remaining
0.0	0.0	0	3890	17,500	4.5	1.00
0.5	48.8	1900	1980	15,600	7.9	0.89
1.5	59.1	2300	1630	15,200	9.3	0.87
3.5	66.8	2600	1280	14,900	11.6	0.85
5.5	69.4	2700	1160	14,800	12.8	0.84
10.5	74.6	2900	960	14,600	15.2	0.83
15.5	77.1	3000	850	14,500	17.0	0.83
30.5	79.7	3100	760	14,400	18.9	0.82
60.5	82.3	3200	690	14,300	20.7	0.82
90.5	84.8	3300	620	14,200	22.9	0.81

As a result of this oxygen excess, a consistent influence of oxygen partial pressure on waste destruction was not demonstrated. This is illustrated in figures 11 through 14, comparing air versus oxygen for different waste types. The air results are based on a 500 lb/in<sup>2</sup> charge at ambient temperature, while the oxygen results consist of combinations of pressures ranging from 100 to 500 lb/in<sup>2</sup>.

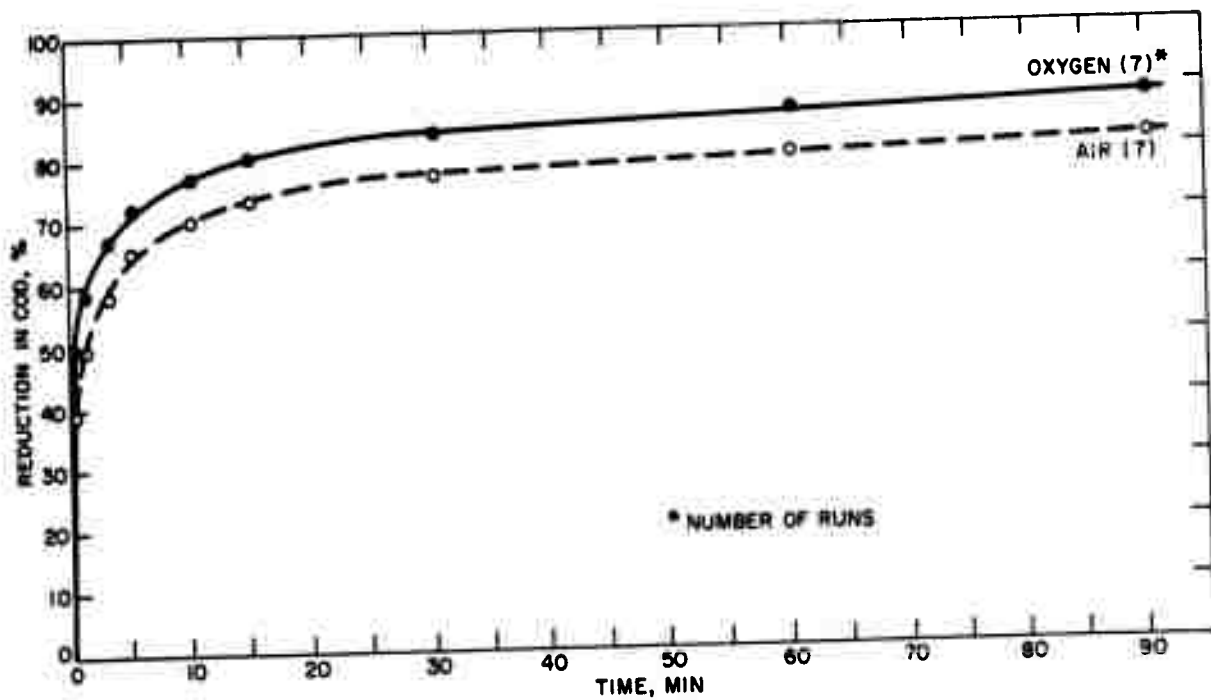


Figure 11  
Wet Oxidation of Primary Sludge  
at 500° F (Combined Runs)  
Air Versus Oxygen

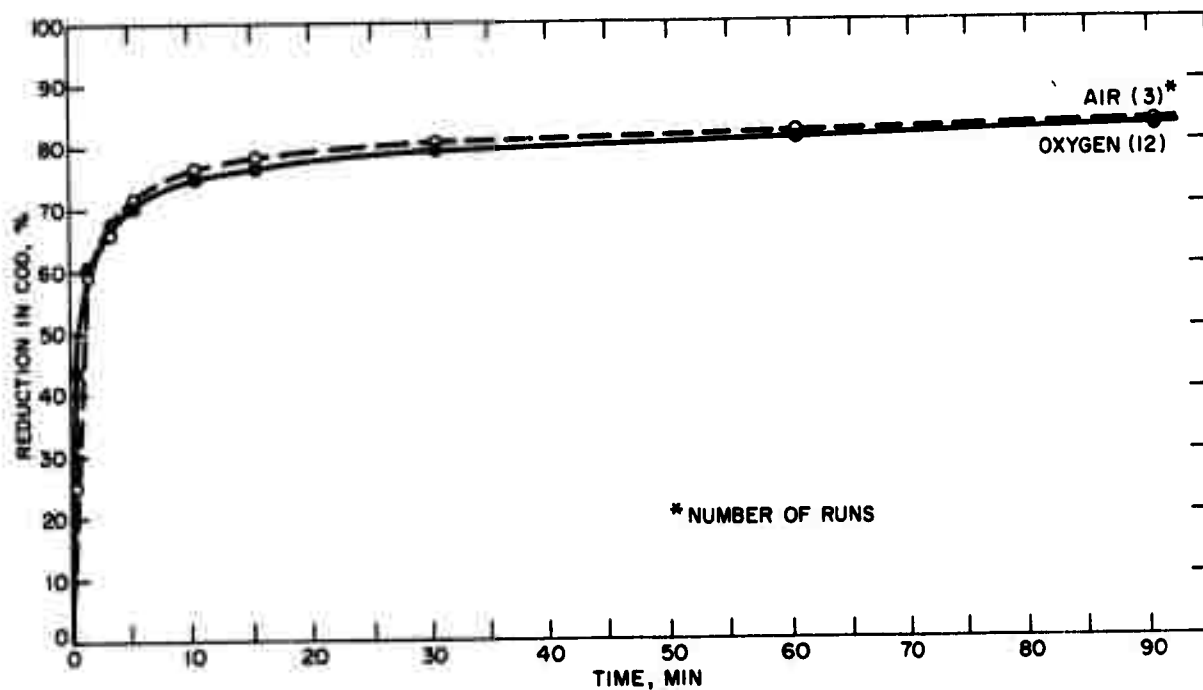


Figure 12  
Wet Oxidation of Glucose at  
500° F (Combined Runs)  
Air Versus Oxygen

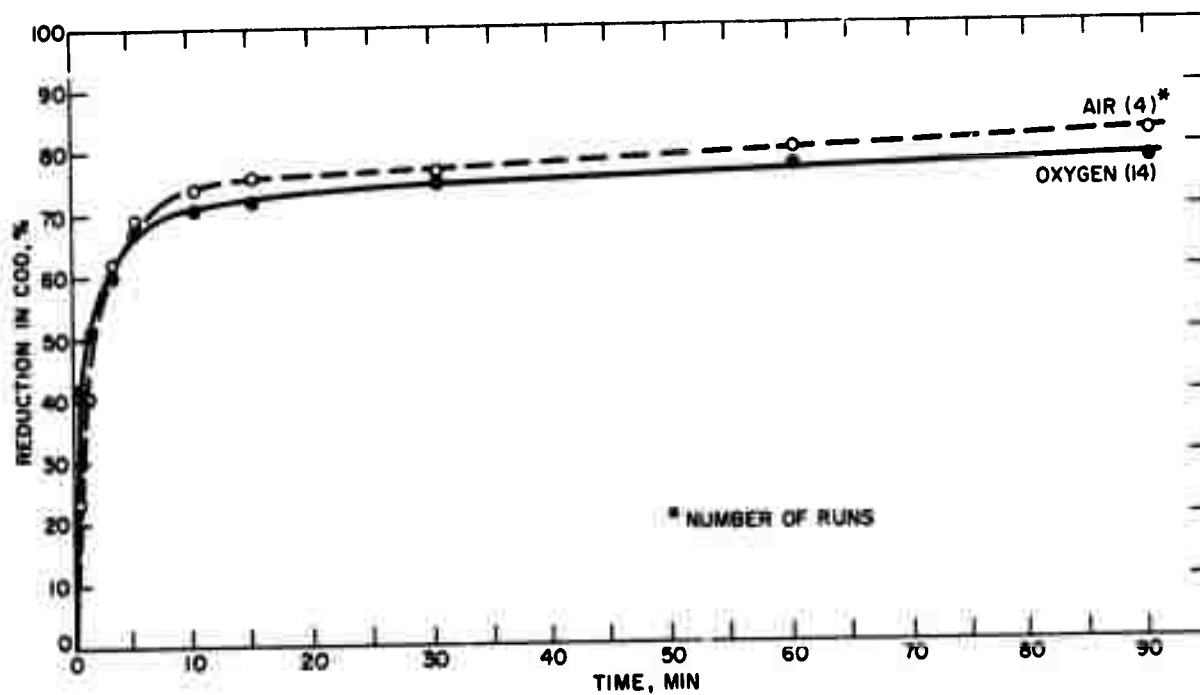


Figure 13  
Wet Oxidation of Oil-in-Water  
Emulsions at 500° F (Combined Runs)  
Air Versus Oxygen

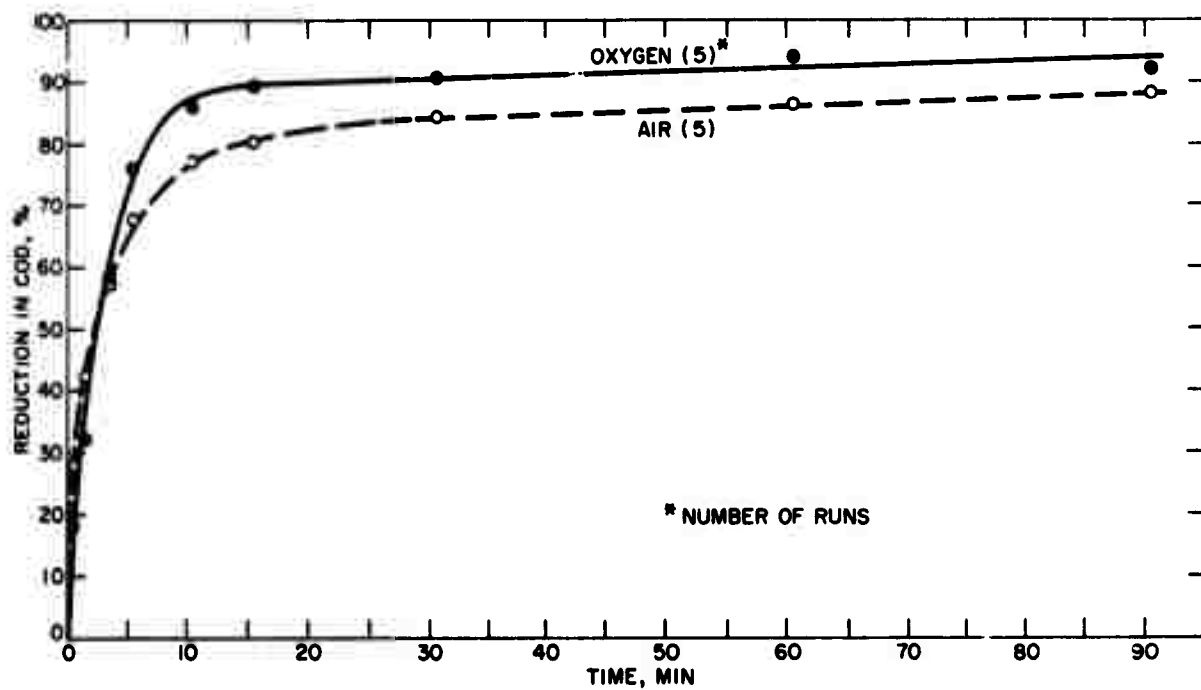


Figure 14  
Wet Oxidation of Cellulose  
at 500° F (Combined Runs)  
Air Versus Oxygen

## INFLUENCE OF TEMPERATURE

Figure 15 illustrates the effect of varying the wet oxidation reaction temperature from 500° to 600° F when processing primary sludge.

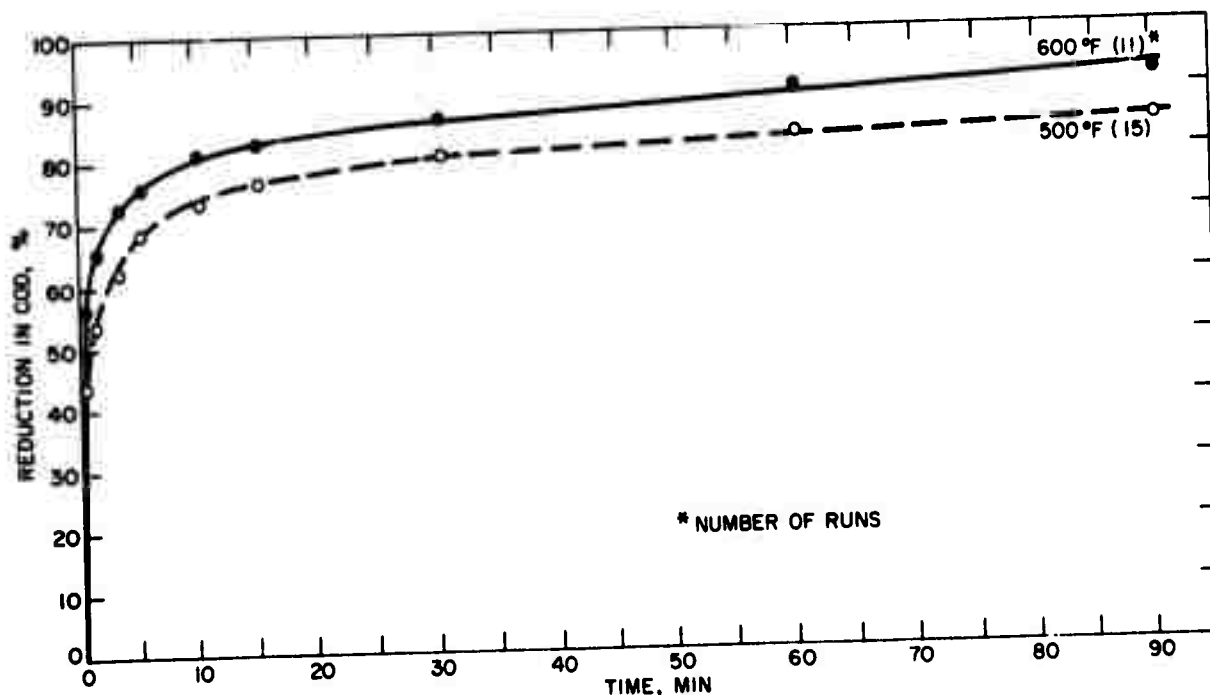


Figure 15  
Wet Oxidation of Primary Sludge  
(Combined Runs) Effect of Reaction Temperature

An increased reduction in COD of approximately 7% is achieved by increasing the reaction temperature 100° F. This incremental improvement at the higher temperature is not sufficient to accept the substantially higher operating pressure which results. Table 8 shows that the saturated steam pressure more than doubles, increasing from 680 lb/in<sup>2</sup> at 500° F to 1545 lb/in<sup>2</sup> at 600° F.

TABLE 8  
OPERATING PRESSURES FOR THE AUTOCLAVE

Pressure	Autoclave Temperature, ° F			
	450	500	550	600
Precharge, lb/in <sup>2</sup> g				
100	170	180	190	200
200	340	360	380	400
300	515	540	570	595
400	685	720	760	795
500	855	900	950	995
750	1280	1350	1425	1490
Saturated steam, lb/in <sup>2</sup> a	425	680	1020	1545
Note: The precharge pressure at operating temperature is found by taking the value at the intersection of the appropriate row and column. Adding the saturated steam pressure to this yields the total operating pressure of the autoclave.				

#### INFLUENCE OF pH

Addition of sulfuric acid, reducing the initial pH to 2, was investigated with the concentrated sanitary waste. Results are shown in figure 16, which illustrates that acid addition gives no advantage in oxidizing this waste.

Measurement of pH was carried out on a number of samples taken from the autoclave. Results are presented graphically in figures 17 through 20, showing pH versus wet oxidation reaction time for different feed types. The initial pH is that for the waste mixture as it would exist under ambient, nonoxidizing conditions. All figures show a rapid increase in acidity from an essentially neutral initial condition. This increase in acidity is attributed to the formation of low molecular weight carboxylic acids and carbon dioxide. Some rise in pH after the initial drop (30-second sample) is observed in all cases, but it is very small for cellulose and oil, and more pronounced in the case of primary sludge. Recovery of pH in the case of the primary sludge experiments is attributed primarily to the slow hydrolysis of organic nitrogen to ammonia.



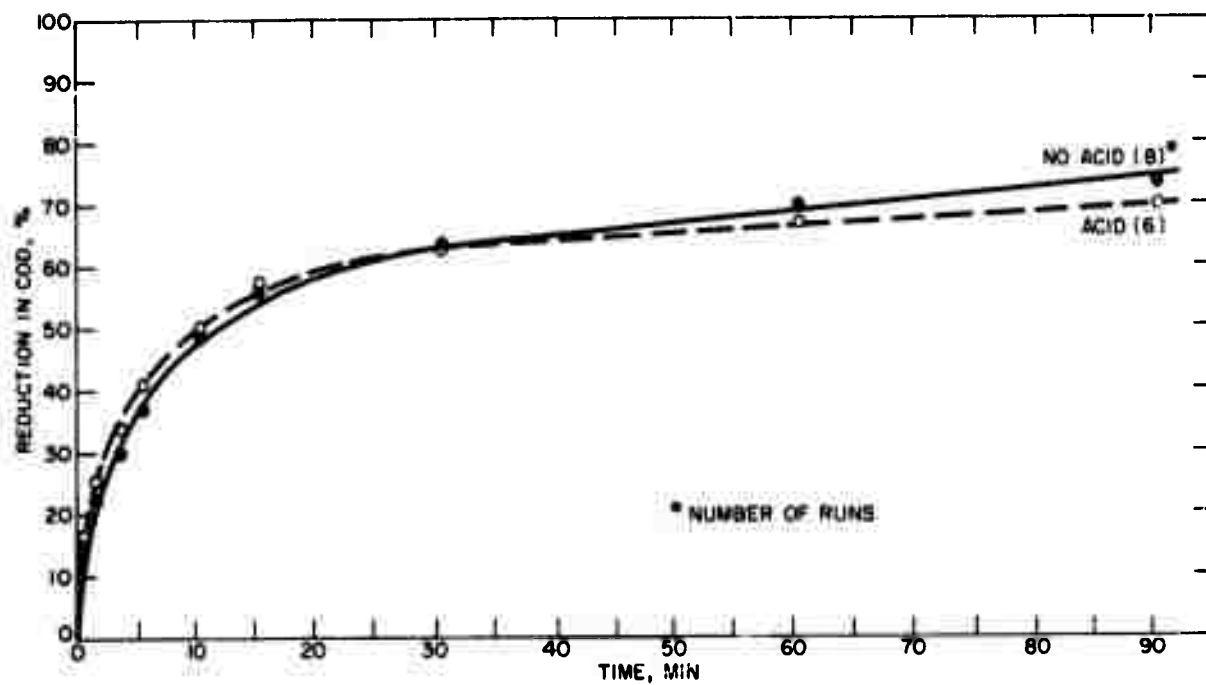


Figure 16  
Wet Oxidation of Concentrated Sanitary Waste  
at 500° F (Combined Runs)  
Acid Versus No Acid Addition

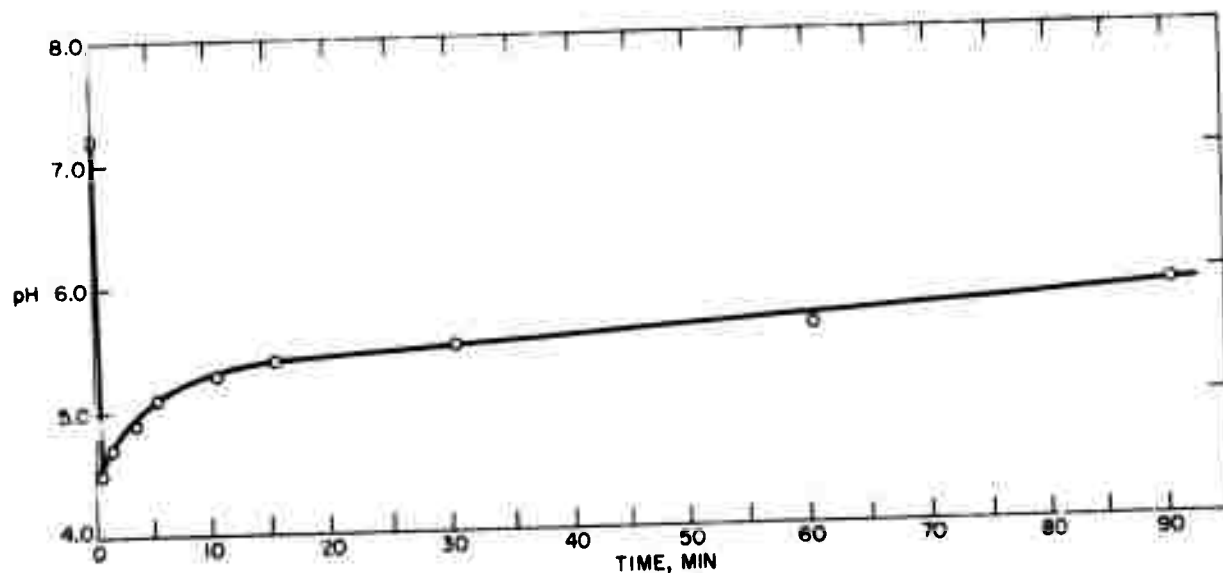


Figure 17  
Acidity Changes During Wet Oxidation Reactions  
(Primary Sludge, 20 Runs,  
500° and 600° F Data Combined)

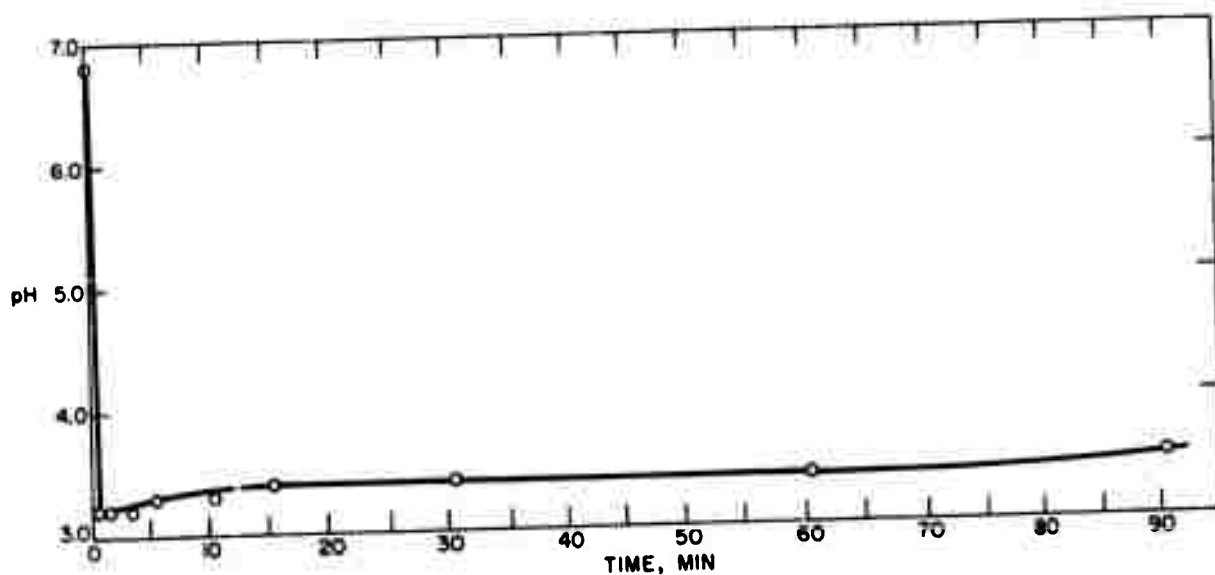


Figure 18  
Acidity Changes During Wet  
Oxidation Reactions  
(Oil-in-Water Emulsions, 500° F, 3 Runs)

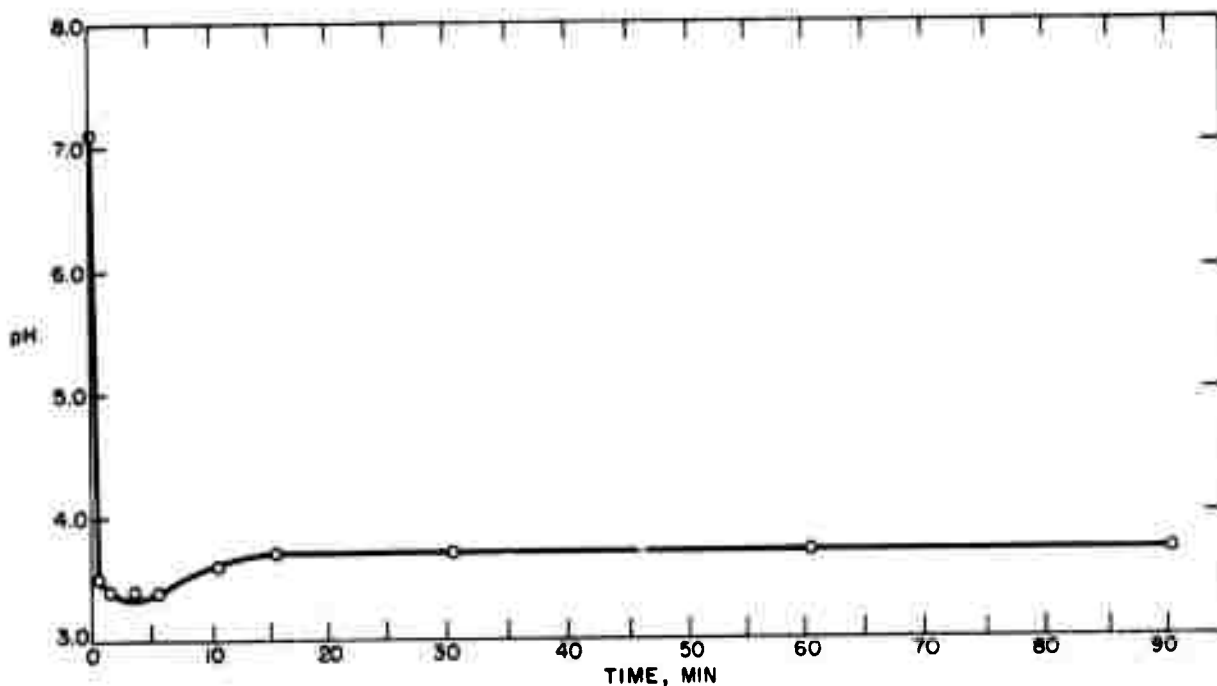


Figure 19  
Acidity Changes During Wet Oxidation Reactions  
(Cellulose, 500° F, 14 Runs)

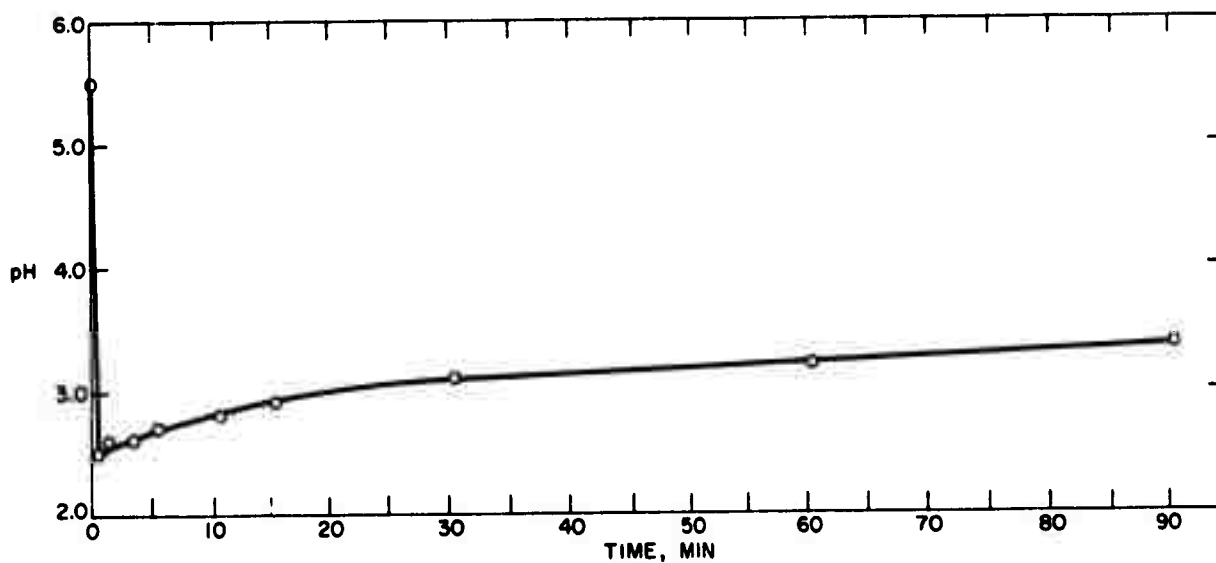


Figure 20  
Acidity Changes During Wet Oxidation Reactions  
(Glucose, 500° F, 3 Runs)

## INFLUENCE OF SALT CONCENTRATION

To illustrate the influence of salt concentration, experiments were conducted with glucose in distilled water and in synthetic sea water (3.5% salt content) prepared in accordance with ASTM method D-1141-52. Figure 21 shows no effect attributable to salt content.

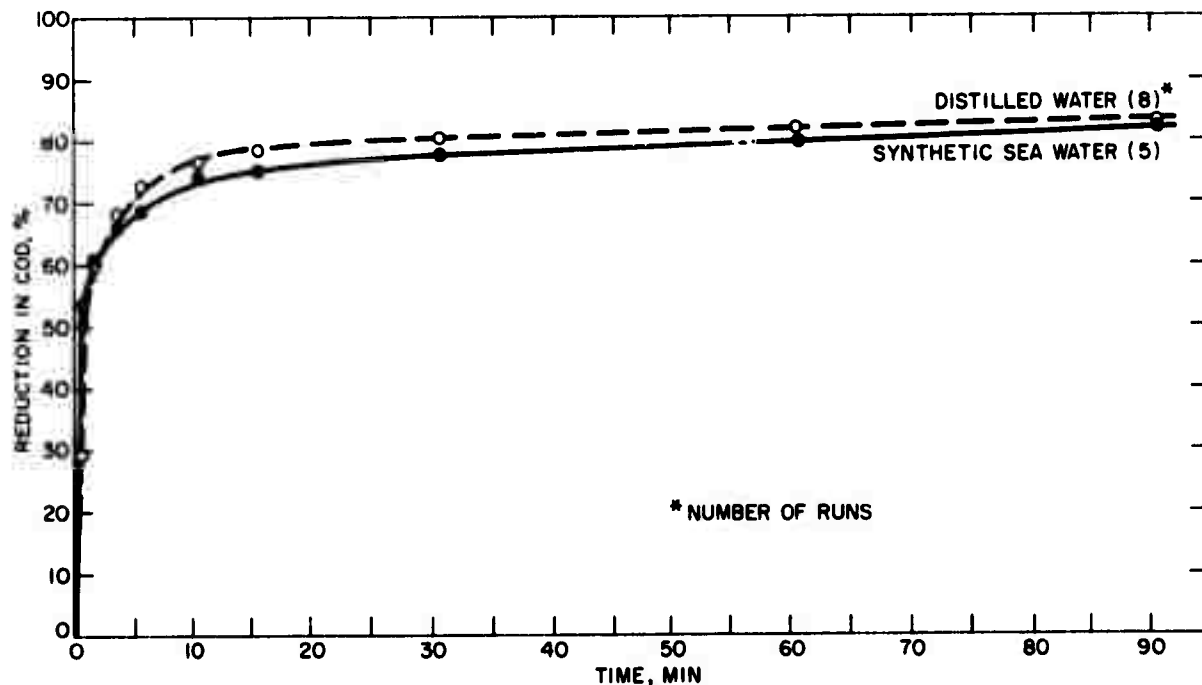


Figure 21  
Wet Oxidation of Glucose at 500° F (Combined Runs)  
Effect of Synthetic Sea Water

## INFLUENCE OF CATALYSTS

All foregoing experiments were conducted without the deliberate addition of materials that could serve to catalyze the reaction. An autocatalytic effect might occur during the rapid portion of the reaction as a result of the sharp drop in pH. The influence of catalysis was examined as part of a sponsored effort under contract.<sup>5</sup> Some results of this effort are presented in this report.

Experiments conducted were very similar in apparatus and procedure to those reported thus far. A 1-gallon autoclave (Autoclave Engineers, Inc.) was used, operating temperature was 475° F, but larger volumes of waste feed could be injected resulting in higher initial values for  $C_0$ . Sulfuric acid was added, reducing the pH to 1.5-2.0; a proprietary catalyst was used; and the pressure vessel was lined with ceramic tile or carbon. Waste feeds used were a primary underflow sludge from a domestic sewage treatment plant and a concentrated sanitary waste consisting of fecal matter, urine, and paper.

Results are presented in table 9 along with data from an earlier section of this report for comparison. Graphical presentation of the data is given in figures 22 and 23. Figure 22 illustrates that ceramic tile and carbon lining have an equal and significant effect in enhancing the rate of wet oxidation. Figure 23 shows a noticeable influence of the catalyst on the rate of wet oxidation.

TABLE 9 - CATALYTIC EFFECTS DURING WET OXIDATION

Reduction in COD after (%)		Initial COD mg/l	$k_1$ , min <sup>-1</sup>	$k_2$ , min <sup>-1</sup>	Number of Runs	Special Conditions
15 Min	60 Min					
Concentrated Sanitary Waste						
80	90	37,000	0.08	0.002	1	Unlined, catalyst, acid
92	96	37,000	0.20	0.011	1	Carbon lined, catalyst, acid
92	95	41,000	0.29	0.011	1	Tile lined, catalyst, acid
56	70	1,310-1,980	0.06	0.008	8	None
Primary Sludge Waste						
73	87	15,400	0.03	0.009	1	Carbon lined, no catalyst, acid
81	91	10,700	0.05	0.006	1	Carbon lined, catalyst, acid
76	83	1,720-3,890	0.12	0.007	15	None

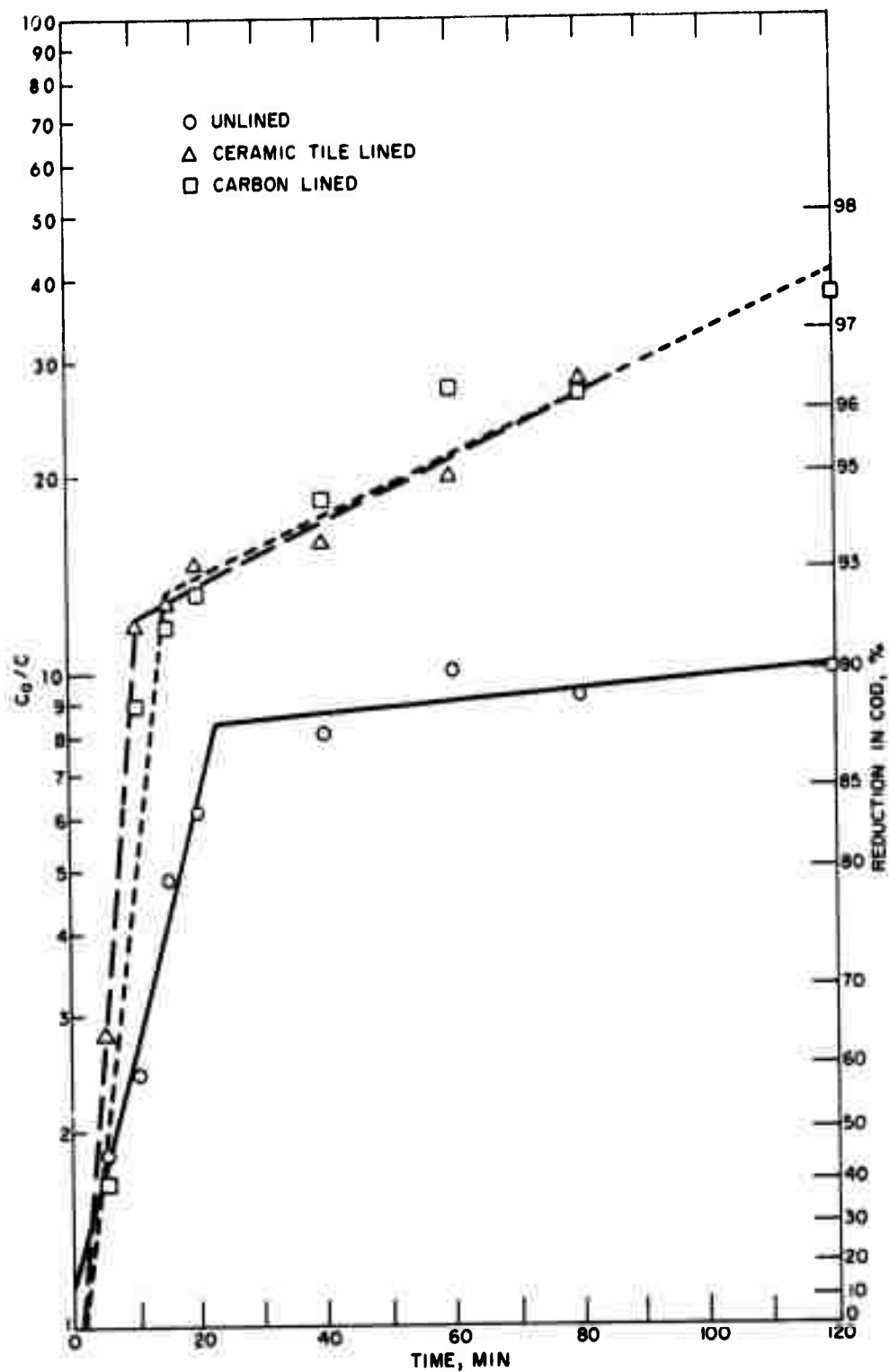


Figure 22 - Catalytic Effects  
During Wet Oxidation of Concentrated Sanitary Waste  
(475° F, Catalyst Present, Acid Added)

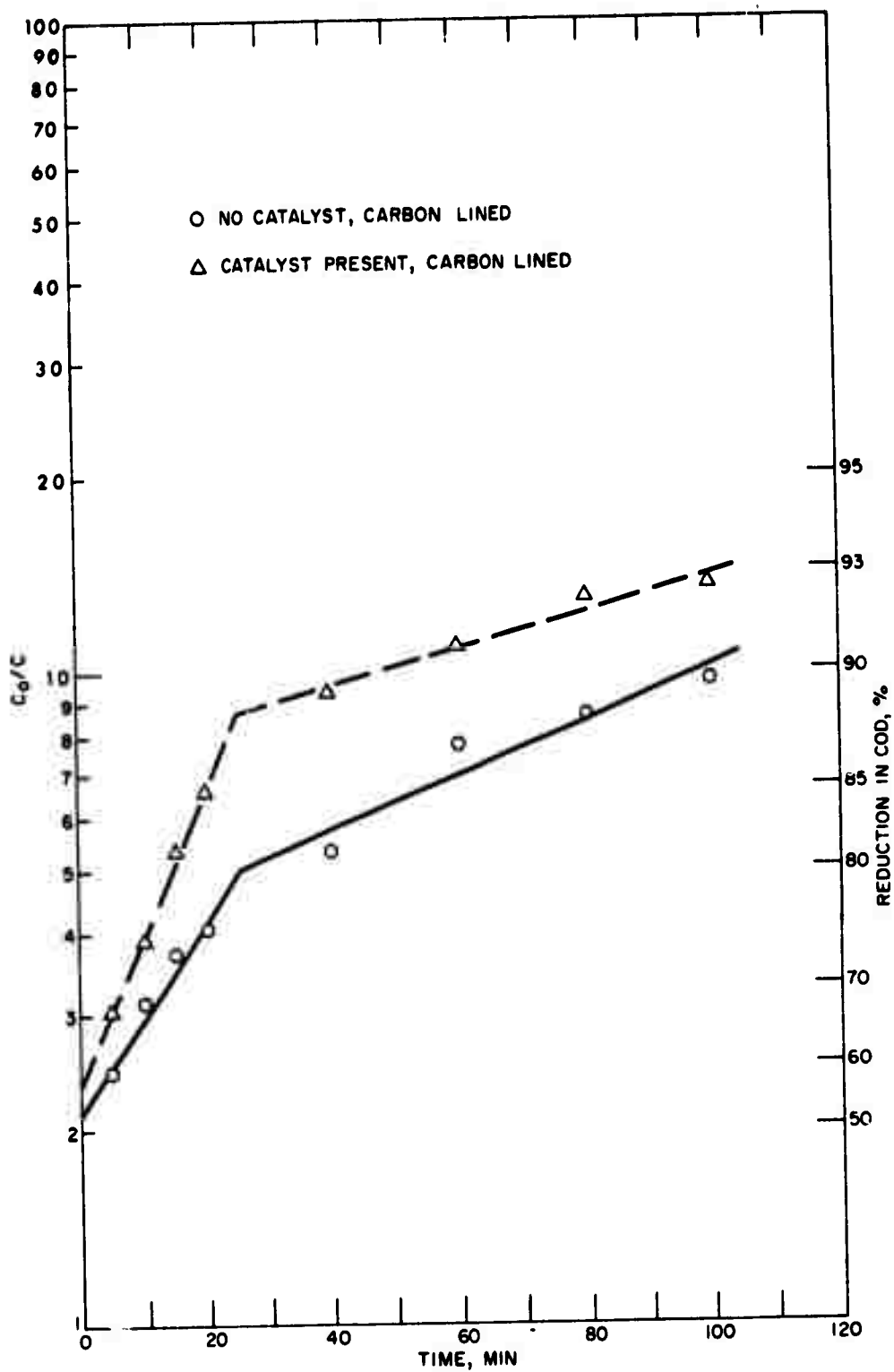


Figure 23 - Catalytic Effects  
During Wet Oxidation Primary Sludge  
(475° F, Acid Added)

## REVERSE OSMOSIS AS A POSTTREATMENT PROCESS FOR WET OXIDATION

To evaluate the effectiveness of reverse osmosis (RO) as a posttreatment step to wet air oxidation, product effluent collected from the autoclave after 90 minutes at 500° F was passed through an RO cell equipped with a cellulose acetate membrane operated at 400 lb/in<sup>2</sup>. A schematic of the RO system is shown in figure 24. Results shown in table 10 illustrate that RO can serve as an effective posttreatment step for wet oxidation effluents.

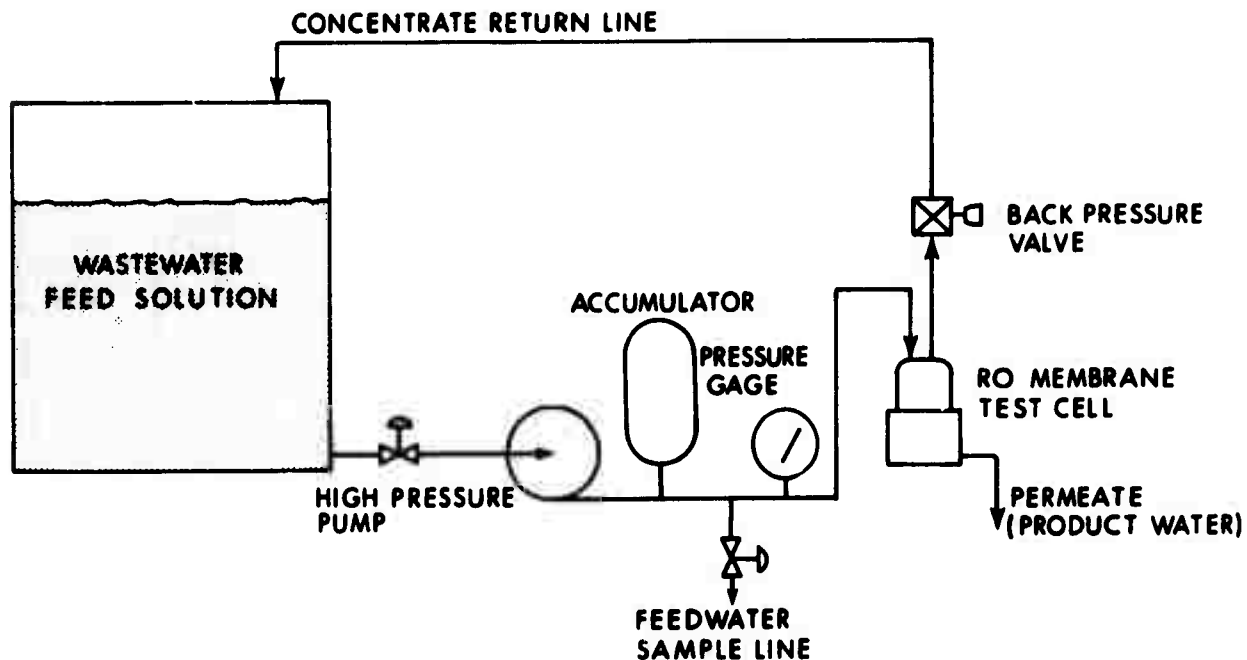


Figure 24  
Wastewater System Used to Evaluate  
Performance of Reverse Osmosis Membranes



TABLE 10  
REVERSE OSMOSIS OF WET OXIDATION EFFLUENT

Waste Feed Producing Effluent	RO Flux Rate gal/ft <sup>2</sup> /d	COD, mg/l		COD Reduction (%)
		Wet Oxida- tion Effluent	RO Effluent	
Oil-in-water	8.4	1120	540	51
Primary sludge	9.1	355	155	56
Concentrated sanitary	7.0	385	70	82

### DISCUSSION

For ultimate disposal of shipboard aqueous organic wastes, wet oxidation is unique in that:

- It produces a sterile liquid usable as a process fluid with no or minimal posttreatment.
- It operates at temperatures substantially below those required for incineration.
- It can be thermally self-sustaining after start-up.
- It operates at pressures similar to those used for steam turbine propulsion systems.
- It produces essentially no air pollutants.
- It is particularly suitable where space is at a premium.

The effectiveness of wet oxidation is often measured in terms of the percent reduction in COD and how this reduction is affected by temperature, time, catalysis, and oxygen utilization. While this is useful, it can be misleading. Aqueous wastes, such as sanitary, laundry, and galley, are pollutants not only because they lower the oxygen content of waters containing marine life, but also because they are in various stages of decay and carry disease-causing organisms. Exposure to wet oxidation conditions for 10 minutes destroys all organisms, converts a large percentage of the organic waste to carbon dioxide and water, and converts the rest to inoffensive, soluble, easily biodegradable, low molecular weight organic compounds.

Between 300° and 500° F, temperature plays a significant role on the effectiveness of wet oxidation. This has been illustrated for various sanitary sludges. Thus, an eightfold increase in reduction of COD was found from 300° to 500° F.<sup>12</sup> Above 500° F, or even at 475° F, a leveling-off effect is observed.<sup>12</sup> This is confirmed by results shown in figure 15; namely, the additional waste destruction obtained at 600° versus 500° F is small. This reduced effect of temperature on sludge destruction is caused by the rapid conversion of the wastes at these higher temperatures to low molecular weight organic acids which oxidize at rates 30 to 40 times slower, as illustrated in table 3. Consequently, it is not practical to operate wet oxidation above 500° F, because the additional waste destruction does not warrant the penalty of the substantial increase in steam pressure. Such an increase in steam pressure would not only require a heavier pressure vessel but a larger air compressor.

Examination of the reaction rates for a variety of wastes has convincingly demonstrated the presence of at least two major reaction stages. The first stage, or fast reaction, is 30 to 40 times faster than the second major stage of the reaction. This has important implications with regard to design of wet oxidation pressure vessels. The drop in pH during the initial portion of the reaction is an independent measure of the rapid events occurring in the wet oxidation process.

Catalysts appear to enhance the wet oxidation process. The main advantage of catalysts is to permit operation of the process at lower temperatures without loss of effectiveness. Reducing operating temperature and therefore pressure implies a smaller, lighter reaction pressure vessel and air compressor. Use of catalysts, however, carries a potential penalty. If the catalyst is dissolved or suspended in the aqueous medium, it is lost upon discharge; further, the catalyst itself may be a pollutant when discharged. If the catalyst is stationary, effective contact between it and the aqueous medium must be maintained. Decline in catalyst potency requiring frequent replacement or regeneration may be expensive and time consuming.

## FUTURE EFFORT

Future effort in wet oxidation will be primarily concerned with the evaluation of a 30-man closed-loop process for treatment of shipboard sanitary waste. This process utilizes a four-compartment agitated autoclave operating at 600 lb/in<sup>2</sup> pressure and 450° F for the destruction of human wastes. Raw waste is passed through the autoclave in a slightly ammoniacal catalyzed aqueous solution (pH 8 to 9) which, after wet oxidation and filtration, is reused as a flushant. Excess water accumulated is exhausted as a vapor and injected into the engine exhaust. The system envelope is approximately 4 x 6 x 3 feet. Evaluation of this system will consist of an extensive laboratory investigation followed by shipboard installation and further performance investigation. Delivery of the unit is expected in September 1974.

## TECHNICAL REFERENCES

- 1 - Ploos Van Amstel, J.J.A., "The Oxidation of Sewage in the Liquid Water Phase at Elevated Temperatures and Pressures," Accession No. N71-34342, National Tech Info Center, Springfield, Va. (1972)
- 2 - Bridges, D. W., and W. M. Fassell, "Pilot-Plant Demonstration of Wet Oxidation for Treatment of Shipboard Wastewaters," final rept on U.S. Coast Guard Contract DOT-CG-31323-A by Barber-Colman Co., Santa Ana, Calif. (Feb 1974)
- 3 - Jagow, R. B., "A Study to Evaluate the Feasibility of Wet Oxidation for Shipboard Waste Water Treatment Application," final rept on U.S. Coast Guard Contract DOT-CG-23034-A by Lockheed Missiles and Space Co., Sunnyvale, Calif. (Jan 1974)
- 4 - U.S. Navy Contract N62477-73-C-0121 to Zimpro, Inc., Rothschild, Wis. (Sep 1973)
- 5 - Fassell, W. M., and D. W. Bridges, "Destruction by Wet Oxidation of Double Base Solid Propellants, Trinitrotoluene, Nitrate Esters, Photographic Film and Shipboard Waste," final report on U.S. Navy Contract N00174-73-C-0140 by Barber-Colman Co., Santa Ana, Calif. (Oct 1973)
- 6 - NASA Contract NAS 1-11748 to Lockheed Missiles and Space Co., Sunnyvale, Calif.
- 7 - "Materials for Wet Oxidation Processing Equipment (Shipboard)," final rept NMAB-312 on DOD Contract DA-49-083 OSA-3131 by National Materials Advisory Board, National Academy of Sciences (Dec 1973)

- 8 - U.S. Navy Contract N00406-74-C-0961 by Naval Supply Center, Puget Sound, to Barber-Colman Co. (Dec 1973)
- 9 - Standard Methods for the Examination of Water and Wastewater, 13th ed.
- 10 - Zoss, L. M., et al, "The Solubility of Oxygen in Water," ASME Paper 53-S-30 (Apr 1953)
- 11 - Pray, H. A., et al, "Solubility of Hydrogen, Oxygen, Nitrogen, and Helium in Water at Elevated Temperatures," Industrial and Engineering Chemistry, Vol. 44, No. 5 (May 1952)
- 12 - Hurwitz, E., et al, "Wet Air Oxidation of Sewage Sludge," Water and Sewage Works, Vol. 112, No. 8, pp. 298-305 (Aug 1965)

## APPENDIX A

### WASTE FEED MATERIALS

#### CELLULOSE

Cellulose feed was prepared by placing weighed sheets of toilet paper in a blender with distilled water. The mixture was macerated for approximately 2 to 3 minutes until the sheets were disintegrated into small fibrous pieces suitable for injection. In spite of this preparation, the cellulose fibers often matted and clogged the injection lines, resulting in failure or partial failure of all the feed to inject.

Cellulose was selected to test in the wet air oxidation unit, since it represents a variety of waste products generated on board ship.

#### GLUCOSE

Stock solutions of glucose were prepared whenever needed by dissolving a known amount of glucose in 1 liter of distilled water. The glucose feed provided an ideal system with which to investigate various parameters of the wet air oxidation process, since it formed a true solution eliminating injection problems and had identical characteristics from one batch of feed to the next.

#### PRIMARY SLUDGE

Domestic sewage sludge was obtained from the Maryland City Sewage Treatment Plant. Samples of sludge were taken from the primary clarifiers' underflow and were refrigerated until needed. The sludge was macerated in a blender prior to placing it in the injection cylinders.

#### OIL

Oil-in-water emulsions were used for feeds to simulate bilge water. The emulsions were prepared by mixing 0.1% or 0.5% oil in water with an ultrasonic mixer to form stable emulsions. The oil used was one designed to emulsify easily.

## TOMATO JUICE

Tomato juice was selected as a feed to simulate a food waste, since it has a high COD value, consists of organic molecules typical of food wastes, and was already in a stable suspension facilitating injection.

## REDUCED FLUSH SANITARY WASTE

The reduced flush sanitary waste came from the vacuum collection tank of the Jered Vacu-Burn sewage treatment system (STS) This is an STS designed for shipboard use and operates with a significantly reduced volume of flushing water. The sludge consists entirely of human waste (feces and urine) and toilet paper in concentrated form.

## APPENDIX B

### DETAILED OPERATING PROCEDURE

An appropriate amount of distilled water is added to the pressure vessel via the blowpipe, and a known overpressure of either oxygen or air is then added from the precharge gas cylinders. The temperature controller is then set for the desired temperature and turned on.

As the pressure vessel attains operating temperature, the feed material is prepared and placed in the injection cylinders, normally with 100 ml of distilled water in the final cylinder as a line flush during injection. When operating temperature is reached, the magnetic stirrer is turned on and the feed injected utilizing high-pressure air.

At 30 seconds after injection, the first sample is taken via the sample tube and ice-water-cooled condenser. Eight more samples are taken at 1.5, 3.5, 5.5, 10.5, 15.5, 30.5, 60.5, and 90.5 minutes after injection.

Upon completion of an experiment, the remaining liquid in the pressure vessel is removed through the blowpipe. The injection cylinders, feed lines, and pressure vessel are all flushed with distilled water prior to beginning the next experiment.

APPENDIX C

RATE OF REDUCTION IN CHEMICAL OXYGEN DEMAND  
FOR VARIOUS WET OXIDATION RUNS

C-i.



TABLE 1-C - PRIMARY SLUDGE, 500° F, AIR OR OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
11272A	41.4	53.1	58.4	66.7	68.9	74.1	78.1	82.6	84.4	1720
11272B	37.8	50.3	59.8	68.5	71.0	72.1	77.2	79.7	81.0	2030
11222	34.8	46.7	58.7	64.5	73.6	77.8	82.4	85.3	87.0	3230
11202	64.6	75.4	83.6	88.0	85.1	88.5	91.0	93.9	95.9	3090
11172B	52.6	63.1	70.7	77.5	80.7	83.1	85.4	87.8	89.1	3550
11172A	54.3	63.2	70.5	75.6	78.8	80.9	83.7	86.1	87.5	3350
11152E	48.2	59.6	68.4	74.5	79.0	81.1	83.4	85.7	87.2	3600
11132B	60.0	61.9	68.4	72.1	77.0	79.3	82.5	85.0	86.4	3780
11132A	60.3	66.1	72.4	75.2	79.6	81.3	84.6	86.6	87.7	3640
11102	49.0	58.1	67.1	70.3	75.4	78.1	80.5	82.2	84.0	3890
11092	49.6	56.2	61.9	69.8	73.9	77.0	79.2	79.6	80.7	3560
11062	32.2	41.0	51.0	57.7	64.4	67.8	71.7	75.7	77.0	1860
11022	37.2	48.0	58.3	63.4	69.2	72.8	76.8	79.7	80.7	1960
10312	15.0	28.5	39.6	48.7	57.9	63.0	69.8	72.8	76.0	1880
10162	19.9	32.6	44.9	53.0	62.8	69.6	75.7	80.4	83.3	1940
Mean	43.8	53.6	62.2	68.4	73.2	76.4	80.1	82.9	84.5	
Standard deviation	14.5	12.7	11.3	10.4	7.5	6.6	5.5	5.2	5.1	

TABLE 2-C - PRIMARY SLUDGE, 500° F, OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
11132B	60.0	61.9	68.4	72.1	77.0	79.3	82.5	85.0	86.4	3780
11132A	60.3	66.1	72.4	75.2	79.6	81.3	84.6	86.6	87.7	3640
10162	19.9	32.6	44.9	53.0	62.8	69.6	75.7	80.4	83.3	1940
11222	34.8	46.7	58.7	64.5	73.6	77.8	82.4	85.3	87.0	3230
11202	64.6	75.4	83.6	88.0	85.1	88.5	91.0	93.9	95.9	3090
11172B	52.6	63.1	70.7	77.5	80.7	83.1	85.4	87.8	89.1	3550
11172A	54.3	63.2	70.5	75.6	78.8	80.9	83.7	86.1	87.5	3350
Mean	49.5	58.4	67.0	72.3	76.8	80.1	83.6	86.4	88.1	
Standard deviation	16.2	14.2	12.2	11.0	7.1	5.7	4.5	4.0	3.9	

TABLE 3-C  
PRIMARY SLUDGE, 500° F, AIR

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
11272B	37.8	50.3	59.8	68.5	71.0	72.1	77.2	79.7	81.0	2030
11272A	41.4	53.1	58.4	66.7	68.9	74.1	78.1	82.6	84.4	1720
11152B	48.2	59.6	68.4	74.5	79.0	81.1	83.4	85.7	87.2	3600
11092	49.6	56.2	61.9	69.8	73.9	77.0	79.2	79.6	80.7	3560
11102	49.0	58.1	67.1	70.3	75.4	78.1	80.5	82.2	84.0	3890
11062	32.2	41.0	51.0	57.7	64.4	67.8	71.7	75.7	77.0	1860
10312	15.0	28.5	39.6	48.7	57.9	63.0	69.8	72.8	76.0	1880
Mean	39.0	49.5	58.0	65.2	70.0	73.3	77.1	79.7	81.4	
Standard deviation	12.4	11.2	10.0	8.9	7.1	6.3	4.8	4.4	4.0	

TABLE 4-C  
PRIMARY SLUDGE, 600° F, AIR OR OXYGEN

Run No.,	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
11162	72.2	77.8	81.4	83.0	85.2	86.5	89.4	94.3	93.8	3940
11152A	71.8	77.4	81.1	83.3	86.0	87.0	90.3	92.4	93.2	3610
11142	71.5	74.7	77.2	78.5	82.4	83.5	86.0	88.3	86.9	3480
10182	41.7	57.4	66.2	70.8	76.4	79.9	86.0	92.9	96.0	2040
09222	53.5	64.2	72.1	75.0	79.1	82.0	85.9	89.4	90.8	2560
08252	69.4	74.2	77.8	81.5	84.7	85.8	88.4	88.9	92.3	17180
08152	56.8	60.2	72.8	74.5	79.8	81.4	86.2	90.1	92.4	2240
08112	53.8	57.2	67.2	70.2	76.3	-	83.5	88.6	89.8	1110
08102	46.7	63.2	70.8	76.1	78.7	81.9	85.0	89.3	90.8	6890
08082	43.5	58.2	67.8	72.9	77.8	80.8	85.1	89.3	94.7	2080
08072	39.8	54.4	64.1	69.3	74.9	77.6	82.4	87.5	88.5	2440
Mean	56.4	65.4	72.6	75.9	80.1	82.6	86.2	90.2	91.8	
Standard deviation	12.8	8.9	6.0	5.1	3.9	3.0	2.4	2.3	2.7	

TABLE 5-C  
OIL-IN-WATER EMULSION, 500° F, AIR OR OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
01293B	63.1	71.1	76.6	79.5	82.3	83.7	84.5	85.8	87.1	4,310
01293A	66.1	72.4	78.9	80.0	80.6	84.0	84.8	86.3	87.3	3,530
01263B	60.2	65.7	72.1	75.5	78.7	80.1	81.6	83.3	84.4	4,160
01263A	42.4	50.6	58.8	63.3	67.3	69.8	72.3	75.5	75.5	2,810
01243	44.5	53.2	55.9	65.2	69.0	70.0	73.5	76.5	77.5	2,950
01233	43.1	62.3	71.0	74.6	75.6	77.1	78.7	80.3	81.8	10,870
01223B	47.0	61.1	72.1	74.2	76.5	78.0	79.6	81.1	82.8	11,780
01223A	50.1	60.8	70.4	70.4	75.2	76.3	78.1	78.2	78.1	10,690
01193B	32.9	57.3	64.7	69.1	70.2	69.6	74.4	75.7	77.3	9,050
01193A	26.8	45.8	68.4	75.2	79.7	81.1	81.1	84.0	84.5	10,970
01183	40.6	57.3	76.5	81.1	84.9	86.0	86.7	87.5	88.2	12,850
01163	5.4	31.9	64.1	72.5	76.4	78.2	80.3	-	83.4	7,670
01103A	38.1	42.3	48.4	56.7	66.0	67.0	73.2	-	74.2	9,700
01093B	16.4	16.4	42.8	51.6	59.3	60.4	65.9	67.0	67.0	8,920
01093A	23.5	30.5	37.4	-	60.0	60.0	63.5	68.7	68.7	11,280
01083	18.9	25.3	33.8	44.5	59.4	59.4	61.6	65.8	66.9	9,300
01043B	37.9	46.0	58.9	64.1	68.1	70.7	72.1	76.2	77.7	8,380
01043A	19.9	27.0	38.8	48.2	54.1	57.6	62.3	68.2	71.7	8,630
Mean	37.6	48.7	60.5	67.4	71.3	72.7	75.2	77.5	78.6	
Standard deviation	16.8	16.7	14.6	11.3	9.0	9.1	7.9	7.1	6.9	

TABLE 6-C - OIL-IN-WATER EMULSION, 500° F, AIR

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
01193A	26.8	45.8	68.4	75.2	79.7	81.1	-	84.0	84.5	10,970
01183	40.6	57.3	76.5	81.1	84.9	86.0	86.7	87.5	88.2	12,850
01163	5.4	31.9	64.1	72.5	76.4	78.2	80.3	-	83.4	7,670
01043A	19.9	27.0	38.8	48.2	54.1	57.6	62.3	68.2	71.7	8,630
Mean	23.2	40.5	62.0	69.3	73.8	75.7	76.4	79.9	82.0	
Standard deviation	14.6	13.7	16.3	14.5	13.6	12.5	12.6	10.3	7.1	

TABLE 7-C - OIL-IN-WATER EMULSION, 500° F, OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
01083	18.9	25.3	33.8	44.5	59.4	59.4	61.6	65.8	66.9	9,300
01193B	32.9	57.3	64.7	69.1	70.2	69.6	74.4	75.7	77.3	9,050
01223A	50.1	60.8	70.4	70.4	75.2	76.3	78.1	78.2	78.1	10,690
01243	44.5	53.2	55.9	65.2	69.0	70.0	73.5	76.5	77.5	2,950
01263A	42.4	50.6	58.8	63.3	67.3	69.8	72.3	75.5	75.5	2,810
01293B	63.1	71.1	76.6	79.5	82.3	83.7	84.5	85.8	87.1	4,310
01293A	66.1	72.4	78.9	80.0	80.6	84.0	84.8	86.3	87.3	3,530
01263B	60.2	65.7	72.1	75.5	78.7	80.1	81.6	83.3	84.4	4,160
01233	43.1	62.3	71.0	74.6	75.6	77.1	78.7	80.3	81.8	10,870
01223B	47.0	61.1	72.1	74.2	76.5	78.0	79.6	81.1	82.8	11,780
01093B	16.4	16.4	42.8	51.6	59.3	60.4	65.9	67.0	67.0	8,920
01093A	23.5	30.5	37.4	-	60.0	60.0	63.5	68.7	68.7	11,280
01043B	37.9	46.0	58.9	64.1	68.1	70.7	72.1	76.2	77.7	8,380
01103	38.1	42.3	48.4	56.7	66.0	67.0	73.2	-	74.2	9,700
Mean	41.7	51.1	60.1	66.8	70.6	71.9	74.6	77.0	77.6	
Standard deviation	15.4	17.2	14.7	10.8	7.8	8.3	7.3	6.6	6.8	

TABLE 8-C - GLUCOSE, 500° F, AIR OR OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
02203	28.3	58.4	63.6	68.7	74.7	76.2	78.0	79.4	80.6	10,660
02213	37.5	64.5	68.4	76.3	80.3	81.9	83.6	84.6	85.4	10,660
02223	9.2	54.8	66.1	70.5	74.2	76.7	79.8	82.0	83.0	10,540
03053B	42.0	51.4	58.0	61.0	67.7	69.3	71.5	74.3	-	10,440
03053A	61.3	66.4	68.6	72.4	75.3	76.9	79.4	81.9	82.8	10,580
03023	51.6	57.4	61.8	64.8	71.1	69.5	75.8	77.8	78.7	10,520
03213	54.0	63.6	70.4	73.5	78.4	79.5	81.0	82.1	83.3	9,030
03223	58.3	67.0	71.8	71.9	77.2	78.2	80.5	82.2	84.1	14,490
03073B	46.3	58.5	-	67.9	72.5	74.6	77.4	79.5	80.8	10,610
03153	52.6	55.5	66.0	68.7	73.9	77.5	81.8	84.3	85.8	11,540
02233	20.2	57.8	66.8	71.0	75.5	77.4	79.1	81.1	82.1	10,660
02263	21.8	57.9	67.0	70.6	73.9	75.9	77.9	79.5	79.5	10,270
03073A	25.4	58.0	67.7	70.0	74.8	76.6	78.6	79.8	79.8	10,470
03123	36.3	63.5	68.8	71.6	75.9	77.8	81.4	83.6	85.0	10,860
03163	57.0	70.1	75.5	79.1	83.1	84.3	85.5	86.7	86.7	14,540
Mean	40.1	60.3	67.2	70.5	75.2	76.8	79.4	81.2	82.7	
Standard deviation	16.2	5.2	4.3	4.3	3.7	3.9	3.3	3.0	2.5	

TABLE 9-C - GLUCOSE, 500° F, AIR

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
02203	28.3	58.4	63.6	68.7	74.7	76.2	78.0	79.4	80.6	10,660
02213	37.5	64.5	68.4	76.3	80.3	81.9	83.6	84.6	85.4	10,660
02223	9.2	54.8	66.1	70.5	74.2	76.7	79.8	82.0	83.0	10,540
Mean	25.0	59.2	66.0	71.8	76.4	78.3	80.5	82.0	83.0	
Standard deviation	14.4	4.9	2.4	4.0	3.4	3.2	2.8	2.6	2.4	

TABLE 10-C - GLUCOSE, 500° F, OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
03053B	42.0	51.4	58.0	61.0	67.7	68.3	71.5	74.3	-	10,440
03053A	61.3	66.4	68.6	72.4	75.3	76.9	79.4	81.9	82.8	10,580
03023	51.6	57.4	61.8	64.8	71.1	69.5	75.8	77.8	78.7	10,520
03213	54.0	63.6	70.4	73.5	78.4	79.5	81.0	82.1	83.3	9,030
03223	58.3	67.0	71.8	71.9	77.2	78.2	80.5	82.2	84.1	14,490
03073B	46.3	58.5	-	67.9	72.5	74.6	77.4	79.5	80.8	10,610
03153	52.6	55.5	66.0	68.7	73.9	77.5	81.8	84.3	85.8	11,540
02233	20.2	57.8	66.8	71.0	75.5	77.4	79.1	81.1	82.1	10,660
02263	21.8	57.9	67.0	70.6	73.9	75.9	77.9	79.5	79.5	10,270
03073A	25.4	58.0	67.7	70.0	74.8	76.6	78.6	79.8	79.8	10,470
03123	36.3	63.5	68.8	71.6	75.9	77.8	81.4	83.6	85.0	10,860
03163	57.0	70.1	75.5	79.3	83.1	84.3	85.5	86.7	86.7	14,540
Mean	43.9	60.6	67.5	70.2	74.9	76.4	79.2	81.1	82.6	
Standard deviation	14.7	5.5	4.6	4.5	3.8	4.0	3.4	3.2	2.6	

TABLE 11-C  
GLUCOSE, 500° F, DISTILLED WATER, AIR, OR OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
03163	57.0	70.1	75.5	79.3	83.1	84.3	85.5	86.7	86.7	14,540
03123	36.3	63.5	68.8	71.6	75.9	77.8	81.4	83.6	85.0	10,860
03073A	25.4	58.0	67.7	70.0	74.8	76.6	78.6	79.8	79.8	10,470
02263	21.8	57.9	67.0	70.6	73.9	75.9	77.9	79.5	79.5	10,270
02233	20.2	57.8	66.8	71.0	75.5	77.4	79.1	81.1	82.1	10,660
02223	9.2	54.8	66.1	70.5	74.2	76.7	79.8	82.0	83.0	10,540
02213	37.5	64.5	68.4	76.3	80.3	81.9	83.6	84.6	85.4	10,660
02203	28.3	58.4	63.6	68.7	74.7	76.2	78.0	79.4	80.6	10,660
Mean	29.5	60.6	68.0	72.3	76.6	78.4	80.5	82.1	82.8	
Standard deviation	14.4	5.0	3.4	3.6	3.3	3.1	2.8	2.7	2.7	

TABLE 12-C  
GLUCOSE, 500° F, 3 1/2% SYNTHETIC SEA WATER, OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
03053B	42.0	51.4	58.0	61.0	67.7	69.3	71.5	74.3	-	10,440
03053A	61.3	66.4	68.6	72.4	75.3	76.9	79.4	81.9	82.8	10,580
03023	51.6	57.4	61.8	64.8	71.1	69.5	75.8	77.8	78.7	10,520
03213	54.0	63.6	70.4	73.5	78.4	79.5	81.0	82.1	83.3	9,030
03223	58.3	67.0	71.8	71.9	77.2	78.2	80.5	82.2	84.1	14,490
Mean	53.4	61.2	66.1	68.7	73.9	74.7	77.6	79.7	82.2	
Standard deviation	7.4	6.6	5.9	5.5	4.4	4.9	4.0	3.5	2.4	

TABLE 13-C  
CELLULOSE, 500° F, AIR OR OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
12182B	38.5	46.3	51.8	58.8	68.0	72.0	75.0	76.5	81.3	400
12142B	-	50.3	60.0	68.9	75.8	79.5	83.3	85.6	87.9	420
12142A	10.4	36.9	65.3	72.2	80.9	82.7	87.6	89.6	89.6	450
12112A	5.1	11.4	29.0	48.4	66.7	71.4	77.8	81.8	83.3	490
12062	57.7	66.2	81.6	90.0	94.6	95.4	96.2	96.9	97.3	510
12052	13.5	29.1	61.5	85.8	93.3	93.6	94.1	95.5	93.0	700
12042B	25.5	37.4	68.7	88.1	94.5	95.0	95.5	96.3	96.5	780
12042A	27.6	36.0	51.0	72.0	93.7	94.5	95.1	96.0	96.2	1,440
12192A	9.7	18.1	44.9	61.1	72.0	82.2	82.6	-	85.0	430
12202A	14.8	40.5	65.4	72.9	76.5	81.8	86.2	87.6	88.9	450
Mean	22.5	37.2	57.9	71.8	81.6	84.8	87.3	89.5	89.9	
Standard deviation	16.9	15.6	14.5	13.5	11.4	9.3	7.7	7.3	5.7	

TABLE 14-C  
CELLULOSE, 500° F, AIR

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
12182B	38.5	46.3	51.8	58.8	68.0	72.0	75.0	76.5	81.3	400
12142B	-	50.3	60.0	68.9	75.8	79.5	83.3	85.6	87.9	420
12142A	10.4	36.9	65.3	72.2	80.9	82.7	87.6	89.6	89.6	450
12112A	5.1	11.4	29.0	48.4	66.7	71.4	77.8	81.8	83.3	490
12062	57.7	66.2	81.6	90.0	94.6	95.4	96.2	96.9	97.3	510
Mean	27.9	42.2	57.5	67.7	77.2	80.2	84.0	86.1	87.9	
Standard deviation	24.7	20.2	19.3	15.6	11.3	9.8	8.4	7.7	6.2	

TABLE 15-C  
CELLULOSE, 500° F, OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
12052	13.5	29.1	61.5	85.8	93.3	93.6	94.1	95.5	93.0	700
12042B	25.5	37.4	68.7	88.8	94.5	95.0	95.5	96.3	96.5	780
12042A	27.6	36.0	51.0	72.0	93.7	94.5	95.1	96.0	96.2	1,440
12192A	9.7	18.1	44.9	61.1	72.0	82.2	82.6	-	85.0	430
12202A	14.8	40.5	65.4	72.9	76.5	81.8	86.2	87.6	88.9	450
Mean	18.2	32.2	58.3	75.9	86.0	89.4	90.7	93.8	91.9	
Standard deviation	7.8	8.9	10.0	11.0	10.8	6.7	5.9	4.1	4.9	



TABLE 16-C  
REDUCED FLUSH SANITARY  
500° F, AIR OR OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
04023	6.9	13.6	18.2	25.4	39.0	51.1	63.2	69.1	72.0	1,810
03303	25.7	31.2	37.8	42.6	54.2	62.5	70.1	74.2	76.3	1,840
03293	28.3	36.2	47.2	54.2	63.7	67.7	73.1	78.3	80.3	1,980
04043A	5.0	15.9	26.2	35.3	-		56.7	69.5	73.8	1,680
04043B	16.6	24.0	28.2	35.6	48.0	59.6	66.5	71.8	75.4	1,950
04063	8.7	16.5	24.6	30.2	42.4	47.3	57.3	64.0	68.5	1,310
04093A	10.5	18.0	27.4	34.1	44.6	49.9	60.0	66.4	70.5	1,700
04093B	14.1	22.0	29.9	39.2	49.3	53.4	61.1	65.8	69.6	1,700
Mean	14.5	22.2	29.9	37.1	48.7	55.9	63.5	69.9	73.3	
Standard deviation	8.6	8.0	8.9	8.7	8.2	7.5	5.9	4.7	3.9	

TABLE 17-C  
REDUCED FLUSH SANITARY  
500° F, ACID AND OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
05093	12.8	20.6	27.7	41.2	47.7	56.1	61.7	66.5	70.0	1,330
05103	8.4	18.5	31.0	39.2	51.9	55.5	64.1	67.2	70.1	1,470
05143B	15.2	23.0	34.3	40.5	50.6	56.0	61.7	65.2	69.0	1,390
05143A	23.5	31.9	38.2	43.2	50.0	55.6	60.7	64.8	67.5	1,490
05163B	17.8	19.5	25.3	30.5	41.6	58.8	63.9	69.2	71.9	4,800
05183	20.9	38.6	46.4	51.0	58.7	62.2	66.5	69.3	70.4	5,020
Mean	16.4	25.4	33.8	40.9	50.1	57.4	63.1	67.0	69.8	
Standard deviation	5.5	8.1	7.7	6.6	5.6	2.7	2.1	1.9	1.5	

TABLE 18-C  
TOMATO JUICE  
500° F, AIR OR OXYGEN

Run No.	Reduction in COD, %									Initial COD mg/l
	Sample Time, min									
	0.5	1.5	3.5	5.5	10.5	15.5	30.5	60.5	90.5	
04123	36.8	42.2	52.1	54.0	59.2	63.1	67.9	71.6	74.7	9,090
04133	-	55.0	60.9	63.7	66.9	69.6	72.8	75.0	76.4	10,020
04163	35.3	45.8	52.7	56.8	62.6	65.9	69.6	72.4	73.8	9,200
04173	35.2	46.0	53.6	57.5	64.4	67.6	70.8	73.5	74.8	10,880
04193	42.4	51.1	60.1	64.8	69.8	71.9	74.1	75.7	75.7	10,660
Mean	37.4	48.0	55.8	59.3	64.5	67.6	71.0	73.6	75.4	
Standard deviation	3.4	5.0	4.3	4.7	4.0	3.4	2.5	1.7	1.4	

APPENDIX D

REACTION RATE CONSTANTS FOR VARIOUS  
WET OXIDATION RUNS

D-i.

TABLE 1-D  
REDUCED FLUSH SANITARY  
500° F, AIR OR OXYGEN

Sample No.	$k_1$ min <sup>-1</sup>	$k_2$ min <sup>-1</sup>
04023	0.041	0.009
03303	0.051	0.007
03293	0.089	0.007
04043A	0.074	0.008
04043B	0.048	0.008
04063	0.052	0.009
04093A	0.070	0.008
04093B	0.067	0.006

Mean = 0.06  
Standard deviation = 0.02  
Range = 0.04-0.09

Mean = 0.008  
Standard deviation = 0.001  
Range = 0.006-0.009

TABLE 2-D  
TOMATO JUICE  
500° F, AIR OR OXYGEN

Sample No.	$k_1$ min <sup>-1</sup>	$k_2$ min <sup>-1</sup>
04123	0.066	0.006
04133	0.054	0.004
04163	0.076	0.004
04173	0.080	0.004
04193	0.096	0.003

Mean = 0.07  
Standard deviation = 0.02  
Range = 0.05-0.10

Mean = 0.004  
Standard deviation = 0.016  
Range = 0.003-0.006

TABLE 3-D  
0.1% OIL-IN-WATER EMULSION  
500° F, AIR OR OXYGEN

Sample No.	$k_1$ min <sup>-1</sup>	$k_2$ min <sup>-1</sup>
01293B	0.112	0.004
01293A	0.155	0.004
01263B	0.096	0.004
01263A	0.088	0.003
01243	0.084	0.004

Mean = 0.11

Standard deviation = 0.03

Range = 0.08-0.16

Mean = 0.004

Standard deviation = 0.0004

Range = 0.003-0.004

TABLE 4-D  
0.5% OIL-IN-WATER EMULSION  
500° F, AIR OR OXYGEN

Sample No.	$k_1$ min <sup>-1</sup>	$k_2$ min <sup>-1</sup>
01233	0.150	0.003
01223B	0.158	0.003
01223A	0.104	0.001
01193B	0.139	0.004
01193A	0.217	0.003
01183	0.233	0.003
01163	0.252	0.004
01103A	0.060	0.003
01093B	0.121	0.003
01093A	0.065	0.003
01083	0.074	0.003
01043B	0.111	0.004
01043A	0.087	0.006

Mean = 0.14

Standard deviation = 0.06

Range = 0.06-0.25

Mean = 0.003

Standard deviation = 0.001

Range = 0.001-0.006

TABLE 5-D  
PRIMARY SLUDGE, 600° F, AIR OR OXYGEN

Sample No.	$k_1$ $\text{min}^{-1}$	$k_2$ $\text{min}^{-1}$
11162	0.093	0.012
11152A	0.128	0.006
11142	0.054	0.008
10182	0.130	0.022
09222	0.119	0.009
08252	0.096	0.008
08152	0.115	0.012
08112	0.092	0.011
08102	0.149	0.010
08082	0.140	0.017
08072	0.128	0.010

Mean = 0.11

Standard deviation = 0.03

Range = 0.05-0.15

Mean = 0.011

Standard deviation = 0.005

Range = 0.006-0.022

TABLE 6-D  
PRIMARY SLUDGE, 500° F, AIR OR OXYGEN

Sample No.	$k_1$ $\text{min}^{-1}$	$k_2$ $\text{min}^{-1}$
11272A	0.104	0.008
11272B	0.130	0.005
11222	0.120	0.008
11202	0.209	0.015
11172B	0.142	0.007
11172A	0.121	0.006
11152B	0.136	0.006
11132B	0.075	0.006
11132A	0.093	0.006
11102	0.106	0.005
11092	0.097	0.003
11062	0.093	0.005
11022	0.106	0.005
10312	0.097	0.006
10162	0.104	0.009

Mean = 0.12

Standard deviation = 0.03

Range = 0.08-0.21

Mean = 0.007

Standard deviation = 0.003

Range = 0.003-0.015

TABLE 7-D  
GLUCOSE, 500° F, AIR OR OXYGEN

Sample No.	$k_1$ min <sup>-1</sup>	$k_2$ min <sup>-1</sup>
02203	0.143	0.003
02213	0.167	0.003
02223	0.201	0.007
03053B	0.076	0.004
03053A	0.062	0.004
03023	0.061	0.004
03213	0.105	0.003
03223	0.073	0.004
03153	0.089	0.007
02233	0.179	0.004
02263	0.174	0.004
03073A	0.164	0.004
03123	0.139	0.006
03163	0.134	0.003

Mean = 0.13

Standard deviation = 0.05

Range = 0.06-0.20

Mean = 0.004

Standard deviation = 0.001

Range = 0.003-0.007

TABLE 8-D  
CELLULOSE, 500° F, AIR OR OXYGEN

Sample No.	$k_1$ min <sup>-1</sup>	$k_2$ min <sup>-1</sup>
12182B	-	0.006
12142B	0.079	0.008
12142A	0.238	0.008
12112A	0.108	0.008
12062	0.210	0.008
12052	0.268	0.008
12042B	0.243	0.005
12192A	0.122	0.005
12202A	0.229	0.008
12042A	0.248	0.006

Mean = 0.18

Standard deviation = 0.08

Range = 0.06-0.27

Mean = 0.007

Standard deviation = 0.001

Range = 0.005-0.008